EXHIBIT D

EPA NEW ENGLAND
MODIFIED METHOD 524.2 FOR
VOLATILE ORGANIC COMPOUNDS
IN DRINKING WATER

Exhibit D - Modified 524.2 for Volatile Organic Compounds in Drinking Water

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1.0 SCOPE AND APPLICATION

1.1 The analytical method that follows is designated to analyze low level purgeable volatile organic compounds in surface water, ground water and drinking water in any stage of treatment. This method applies to the regulated, unregulated and additional drinking water compounds listed on the Target Compound List (524.2 TCL, Exhibit C). This method is based on EPA Method 524.2, Rev. 4.0, from Methods for the Determination of Organic Compounds in Drinking Water, EPA-600/4-90/020, August, 1992, and Mandatory Method Modifications, Technical Notes on DW Methods, October, 1994 - Section IV, Modified for Region I.

1.1.1 As indicated on the chain of custody accompanying each sample delivery group (SDG), the target compound list may be designated as all compounds listed in Exhibit C, 524.2 TCL or a subset of those compounds.

1.2 The method includes sample preparation and the actual analysis which is based on a purge and trap gas chromatograph/mass spectrometer (GC/MS) method.

1.3 Problems have been associated with the following compounds analyzed by this method:

- Chloromethane, vinyl chloride, bromomethane, and chloroethane can display peak broadening if the compounds are not delivered to the GC column in a tight band.
- Acetone, hexanone, 2-butanone, and 4-methyl-2-pentanone have poor purge efficiencies.
- 1,1,1-trichloroethane and all the dichloroethanes can dehydrohalogenate during storage or analysis.
- Chloromethane can be lost if the purge flow is too fast.
- Bromoform is one of the compounds most likely to be adversely affected by cold spots and/or active sites in the transfer lines. Response of its quantitation ion (m/z 173) is directly affected by the tuning of the GC/MS to meet the instrument performance criteria for 4-bromofluorobenzene (BFB) at ions m/z 174/176. Increasing the m/z 174/176 ratio may improve bromoform response.

2.0 SUMMARY OF METHOD

2.1 Water

An inert gas is bubbled through a 5 ml (or 25 ml) sample contained in a specifically designed purging chamber at ambient temperature. The purgeable compounds are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the purgeable compounds onto a gas chromatographic column. The gas chromatograph is temperature-programmed to separate the purgeable compounds which are then detected with a mass spectrometer.

2.2 Method Detection Limits

Prior to analysis, method detection limits (MDLs) for all compounds in Exhibit C, 524.2 TCL, must be established in accordance with 40 Code of Federal Regulations, Part 136, Appendix B. All MDL values must be less than or equal to one-third of the CRQL. The MDL study must be conducted using the same specifications as for sample analysis. These specifications include but are not limited to: tune conditions and technical acceptance criteria, initial and continuing calibration conditions and technical acceptance criteria, method blank conditions and technical acceptance criteria, and all instrument operating conditions. The MDL study must be conducted prior to sample analysis, for each alternate column/technique and/or at least annually, whichever, is more frequent. Seven aliquots of reagent water are spiked with all target compounds listed in Exhibit C, 524.2 TCL, at 2 to 5 times the expected MDLs and are analyzed by purge and trap GC/MS. The 5 ml or 25 ml purge vessel may be used to perform the MDL study, but the same size purge vessel must be used throughout to analyze all standards, samples, QC samples and required blanks. All sequential analyses of MDL standards must be reported and used in the resulting MDL values which are calculated. The MDL results are calculated as described in 40 CFR, Part 136, Appendix B and reported as a separate SDG in accordance with Exhibit B. The appropriate Students' t value must be clearly provided with the algorithm used to calculate the MDL values. MDLs shall be determined and reported for each instrument/column and method.

The MDL study must be reported as detailed in Exhibit B. The individual analytical sequence raw data must be provided and these data must be summarized in a table which demonstrates the calculated MDL values. The summarized MDL results table must include the concentration found for each compound in each aliquot, the mean concentration of each compound, the percent recovery of each compound, the standard deviation for each compound, and the Method Detection Limit. The true concentration of the compound in the spike solution must also be provided. The table must list the compounds in the same order as they appear in the target compound list in Exhibit C. In addition, the MDL values for each instrument and method used in reporting results for an SDG shall be submitted with each data package.

The annually determined MDL for an instrument and method shall always be used as the MDL for that instrument/method during that year. If the instrument/method is adjusted in any way that may affect the MDL, the MDL for that instrument/method must be redetermined and the results submitted for use as the established MDL for that instrument/method for the remainder of the year.

3.0 DEFINITIONS

See Exhibit G for a complete list of definitions.

4.0 INTERFERENCES

4.1 Method interference may be caused by impurities in the purge gas, organic compounds out-gassing from the plumbing ahead of the trap, and solvent vapors in the laboratory. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory method and instrument blanks as described in Section 12. The use of non-Polytetrafluoroethylene (PTFE) tubing, non-PTFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

4.2 Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons and methylene chloride) through the septum seal into the sample during storage and handling.

4.3 Contamination by carryover can occur whenever high level and low level samples are sequentially analyzed. To reduce carryover, the purging device and sampling syringe must be rinsed with reagent water between sample analyses. For samples containing large amounts of water-soluble materials, suspended solids, high-boiling compounds, or high purgeable levels, it may be necessary to wash out the purging device with a detergent solution between analyses, rinse it with distilled water, and then dry it in an oven at 105 °C. The trap and other parts of the system are also subjected to contamination; therefore, frequent bakeout and purging of the entire system may be required. After analysis of a sample containing high concentrations of volatile organic compounds, one or more reagent blanks should be analyzed to check for cross-contamination.

4.4 The laboratory where volatile analysis is performed should be completely free of solvents.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis.

5.2 The following analytes covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzene, carbon tetrachloride, chloroform and vinyl chloride. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here, but demonstration of equivalent performance meeting the requirements of this SOW is the responsibility of the Contractor. The Contractor shall document any use of alternate equipment or supplies in the SDG Narrative.

6.1 Glassware

6.1.1 Syringes - 5 ml or 25 ml, gas-tight with shut-off valve. Micro syringes - 10 µl and larger, 0.006 inch ID needle.

6.1.2 Syringe Valve - two-way, with Luer ends (three each), if applicable to the purging device.

6.1.3 Pasteur Pipets - disposable.

6.1.4 Vials and Caps - 2 ml for GC.

6.1.5 Volumetric Flasks.

6.1.6 Bottle - 15 ml, screw-cap, with Teflon cap liner.

6.2 pH Paper - narrow range

6.3 Balances - analytical, capable of accurately weighing ± 0.0001 g, and a top-loading balance capable of weighing 100 g ± 0.01 g. The balances must be calibrated in accordance with ASTM E 617 specifications each 12-hour work shift. The balances must also be annually checked by a certified technician.

6.4 Purge and Trap Device - consists of three separate pieces of equipment: the sample purge chamber, trap, and the desorber. Several complete devices are now commercially available.

6.4.1 The sample purge chamber must be designed to accept 5 ml or 25 ml samples. The gaseous head space between the water column and the trap must have a total volume of less than 15 ml. The purge gas must pass through the water column as finely divided bubbles, each with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column.

6.4.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 inch. The trap must be packed to contain the following minimum lengths of absorbents: (starting from inlet) 0.5 cm silanized glass wool, 1 cm methyl silicone packed coating, 8 cm of 2,6-diphenylene oxide polymer (Tenax-GC, 60/80 mesh), 8 cm of silica gel (Davison Chemical, 35/60 mesh, grade 15 or equivalent), 7 cm of coconut charcoal and 0.5 cm silanized glass wool. If it is not necessary to determine dichlorodifluoromethane, the charcoal can be eliminated and the polymer can be increased to 15 cm. <u>A description of the trap used for analysis shall be provided in the SDG narrative.</u>

6.4.3 The desorber should be capable of rapidly heating the trap to 180 °C. The polymer section of the trap should not be heated higher than 180 °C and the remaining sections should not exceed 220 °C during bakeout mode.

6.4.4 Trap Packing

6.4.4.1 2,6-Diphenylene oxide polymer, 60/80 mesh chromatographic grade (Tenax GC or equivalent).

6.4.4.2 Methyl silicone packing, 3.0 percent OV-1 on Chromasorb W, 60/80 mesh (or equivalent).

6.4.4.3 Silica gel, 35/60 mesh, Davison, grade 15 (or equivalent).

6.4.4.4 Coconut charcoal -- Prepare from Barnebey Cheney, CA-580-26 lot #M-2649 by crushing through 26 mesh screen.

6.4.4.5 The Contractor may choose to use alternate sorbent traps. However, the alternate sorbent trap selected must meet all the method technical acceptance criteria established in the SOW and Exhibit E.

- The trap packing materials must not introduce contaminants which interfere with identification and quantitation of the compounds listed in Exhibit C (524.2 Volatiles).
- The sorbent trap must be able to accept up to the high point calibration standard without becoming overloaded.
- The alternate sorbent trap must be used for the entire analysis; including the MDL study, initial and continuing calibration, and all blank, sample and QC sample analyses. If a new alternate sorbent trap is chosen after the initial MDL study has been completed, then the MDL study must be reanalyzed using that alternate column. The acceptance criteria established in the SOW and Exhibit E must be achieved for all parameters.

6.4.4.5.1 The alternate trap must be designed to optimize performance. Follow manufacturer's instructions for the use of its product. Before use of any trap, other than the one specified in 6.4.2, the Contractor must meet the criteria listed in 6.4.4.5. Once this has been demonstrated, the Contractor must document the trap composition (packing material/brand name, amount of packing material) in each SDG Narrative.

6.4.4.5.2 Manufacturer provided technical information concerning the performance characteristics of the sorbent trap must be included in the MDL Study data package to support the use of the alternate sorbent trap.

6.4.5 The purge and trap apparatus may be assembled as a separate unit or be an integral unit coupled with a gas chromatograph.

6.5 Gas Chromatography/Mass Spectrometer (GC/MS) System

6.5.1 Gas Chromatograph - the gas chromatograph (GC) system must be capable of temperature programming and must maintain an optimal flow rate throughout trap desorption and GC temperature program operations. The system must include or be interfaced to a purge and trap system as specified in Section 6.4 and have all required accessories including syringes, GC columns, gases and routine maintenance items.

6.5.2 Gas Chromatography Columns

A description of the column used for analysis shall be provided in the SDG narrative.

6.5.2.1 Packed columns **must not** be used. Capillary columns **must** be used to achieve the required separation of all isomers listed in the 524.2 TCL.

6.5.2.2 Capillary Columns

6.5.2.2.1 Minimum length 60 m x 0.75 mm ID VOCOL (Supelco) or equivalent fused silica widebore capillary column with 1.5 μm film thickness.

6.5.2.2.2 Minimum length 30 m x 0.53 mm ID DB-624 (J & W Scientific) or equivalent fused silica widebore capillary column with 3 μm film thickness.

6.5.2.2.3 Minimum length 30 m x 0.32 mm ID DB-5 (J & W Scientific) or equivalent fused silica capillary column with 1 μm film thickness.

6.5.2.2.4 Minimum length 75 m x 0.53 mm ID DB-624 (J & W Scientific) or equivalent fused silica widebore capillary column with 3 μm film thickness.

6.5.2.3 The Contractor may choose to use an alternate capillary column. However, the alternate capillary column selected must meet all the method technical acceptance criteria established in the SOW and Exhibit E.

- The GC column must not introduce contaminants which interfere with identification and quantitation of the compounds listed in Exhibit C (524.2 Volatiles).
- The GC column must be able to accept concentrations up to the high point standard of each target compound without becoming overloaded.
- The GC column must provide equal or better resolution of the target compounds than the columns listed above.
- The alternate GC column must be used for the entire analysis, including the MDL study, initial and continuing calibration, and all blank, QC sample and all sample analyses. If a new alternate GC column is chosen after the initial MDL study has been completed, then the MDL study must be reanalyzed using that alternate column. The acceptance criteria established in the SOW and Exhibit E must be achieved for these parameters.

6.5.2.4 The alternate GC column must be designed to optimize performance. Follow manufacturer's instructions for the use of its product. Before use of any column, other than the ones specified in 6.5.2.2, the Contractor must meet the criteria listed in 6.5.2.3. Once this has been demonstrated, the Contractor must document the column used (brand name, length, diameter, and film thickness) in each SDG Narrative.

6.5.2.5 Manufacturer provided technical information concerning the performance characteristics of the GC column must be included in the MDL Study data package to support the use of the alternate column.

6.5.3 The carrier gas and purge gas for routine GC/MS purge and trap applications is helium. High purity gases must be used to ensure a contaminant free GC/MS system. All carrier gas lines must be constructed from stainless steel or copper tubing. Non-polytetrafluoroethylene (PTFE) thread sealants or flow controllers with rubber components are not to be used.

6.5.4 Mass Spectrometer - must be capable of scanning from 35 to 300 amu every 1 second or less utilizing 70 volts (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all the instrument performance acceptance criteria when 25 ng of BFB is injected through the gas chromatograph inlet. The instrument conditions required for the acquisition of the BFB mass spectrum are given in Section 9.

6.5.4.1 The MS scan rate should allow acquisition of at least five spectra while a sample compound elutes from the GC. The purge and trap GC/MS system must be in a room whose atmosphere is demonstrated to be free of all potential contaminants which will interfere with the analysis. The instrument must be vented to the outside of the facility or to a trapping system which prevents the release of contaminants into the instrument room.

6.5.5 GC/MS interface - any gas chromatograph to mass spectrometer interface that produces data which meet the technical acceptance criteria established in the SOW and Exhibit E. Gas chromatograph to mass spectrometer interfaces constructed of all-glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

6.5.6 Data system - a computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage, on machine-readable media, of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits. Also, for the non-target compounds, software must be available that allows for the comparison of sample spectra against reference library spectra. The NIST/EPA/NIH (May 1992 release or later) and/or Wiley (1991 release or later), or equivalent mass spectral library shall be used as the reference library. The most recent release of the reference library must be utilized. The data system must be capable of flagging all data files that have been edited manually by laboratory personnel since every manual edit must be flagged on the quantitation reports.

6.5.7 Magnetic tape storage device - must be capable of recording data and must be suitable for long-term, off-line storage.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

7.1.1 Reagent water - defined as water in which any interferent, target or non-target compound, is not observed at or above the CRQL of the compounds of interest. Reagent water may be generated by passing tap water through a carbon filter bed containing about 453 g (1 lb) of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).

7.1.1.1 A water purification system (Millipore Super-Q or equivalent) may be used to generate reagent water.

7.1.1.2 Reagent water may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the temperature at 90 °C, bubble a contaminant-free inert gas through the water for one hour. While still hot, transfer the water to a narrow-mouth screw-cap bottle and seal with a Teflon-lined septum and cap.

7.1.2 Methanol - pesticide quality or equivalent

7.2 Standards

7.2.1 Introduction

The Contractor must provide all standards to be used with this contract. These standards may be used only after they have been certified according to the procedure described in Exhibit E. The Contractor must be able to verify that the standards are certified by producing the manufacturer's certificates and/or generating the documentation as described in Exhibit E. Manufacturer's certificates of analysis must be retained by the Contractor for the term of the contract and submitted at the completion of the contract performance. The documentation may be requested during an on-site audit.

7.2.2 Stock Standard Solutions

7.2.2.1 Stock standard solutions may be purchased or may be prepared in methanol from pure standard materials.

7.2.2.2 Prepare stock standard solutions by placing about 9.8 ml of methanol into a 10 ml ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes, or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

7.2.2.3 Add the assayed reference material as described below.

7.2.2.3.1 If the compound is a liquid, using a 100 µl syringe, immediately add two or more drops of assayed reference material to the flask, then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

7.2.2.3.2 If the compound is a gas at room temperature, fill a 5 ml valved gas-tight syringe with the reference standard to the 5 ml mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The gas will rapidly dissolve in the methanol.

7.2.2.3.3 The procedure in Section 7.2.2.3.2 may also be accomplished by using a lecture bottle equipped with a Hamilton Lecture Bottle Septum (#86600). Attach Teflon tubing to the side-arm relief valve and direct a gentle stream of the reference standard into the methanol meniscus.

7.2.2.3.4 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. For non-gaseous compounds, calculate the concentration in micrograms per microliter from the net gain in weight. When compound purity is assayed to be 97.0 percent or greater, the weight may be used without correction to calculate the concentration of the stock standard. If the compound purity is assayed to be less than 97.0 percent, the weight must be corrected when calculating the concentration of the stock solution. See Exhibit E (Analytical Standards Requirements). For gaseous compounds, calculate the concentration in micrograms per microliter, using the Ideal Gas Law, taking into account the temperature and pressure conditions within the laboratory.

7.2.2.3.5 Prepare fresh stock standards every two months for gases or for reactive compounds such as styrene. All other stock standards for non-gaseous/non-reactive purgeable compounds must be replaced six months after the preparation date (or the date opened for purchased stock standards). The stock standards must be replaced sooner if the standard has demonstrated signs of degradation or evaporation.

7.2.3 Secondary Dilution Standards

7.2.3.1 Using stock standard solutions, prepare secondary dilution standards in methanol that contain the compounds of interest, either singly or mixed together. Secondary dilution standard solutions should be prepared at concentrations that can be easily diluted to prepare working standard solutions.

7.2.3.2 Prepare fresh secondary dilution standards for gases and for reactive compounds such as styrene every month, or sooner, if standard has degraded or evaporated. Secondary dilution standards for the other purgeable compounds must be replaced six months after the preparation date (or the date opened for purchased standards). The standards must be replaced sooner if the standard has demonstrated signs of degradation or evaporation.

7.2.4 Working Standards

7.2.4.1 System Monitoring Compound (SMC) Spiking Solution

Prepare a system monitoring compound spiking solution containing 1,2-Dichloroethane-d4 and 1,2-dichlorobenzene-d4 in methanol. For 5 ml purge vessels, prepare the SMC spiking solution at a concentration of 2 µg/ml. For 25 ml purge vessels, prepare the SMC spiking solution at a concentration of 10 µg/ml. A 5 µL addition of the appropriate SMC spiking solution into the respective volume (5 or 25 ml) of sample, QC sample, blank or calibration standard shall yield a final concentration of 2 µg/L. Prepare a fresh spiking solution weekly, or sooner if the solution has degraded or evaporated.

7.2.4.2 Matrix Spiking Solution

Prepare a matrix spiking solution in methanol, specific for the purge vessel being used, that contains the following compounds at the concentrations specified below:

Compound	Concentration (µg/ml) Purge Vessel: 5 ml	25 ml
Vinyl Chloride	10	50
Trichloroethene	10	50
1,2-Dichloroethane	10	50
Carbon Tetrachloride	10	50
Benzene	10	50
1,2-Dichloropropane	10	50
Bromoform	10	50
1,1,2-Trichloroethane	10	50
cis-1,3-Dichloroprpene	10	50
Tetrachloroethene	10	50
1,2-Dibromoethane	10	50
1,4-Dichlorobenzene	10	50
2-Hexanone	25	125
Tetrahydrofuran	250	1250

A 5 µL addition of the appropriate matrix spiking solution into the respective volume (5 or 25 ml) of sample shall yield a final concentration of 25 µg/L 2-Hexanone, 250 µg/L Tetrahydrofuran, and 10 µg/L of the remaining analytes. Prepare a fresh spiking solution weekly, or sooner if the solution has degraded or evaporated.

7.2.4.3 Internal Standard (IS) Spiking Solution

Prepare an internal standard spiking solution containing Fluorobenzene and Chlorobenzene-d5 in methanol. For 5 ml purge vessels, prepare the IS spiking solution at a concentration of 2 µg/ml. For 25 ml purge vessels, prepare the IS spiking solution at a concentration of 10 µg/ml. A 5 µL addition of the appropriate spiking solution into the respective volume (5 or 25 ml) of sample, QC sample, blank or calibration standard shall yield a final concentration of 2 µg/L. Prepare a fresh spiking solution weekly, or sooner if the solution has degraded or evaporated.

7.2.4.4 Instrument Performance Check Solution - 4-Bromofluorobenzene (BFB)

Prepare a 25 ng/µL solution of BFB in methanol. Introduce 25 ng of BFB into the GC either by purging spiked reagent water or by direct injection. Prepare a fresh BFB solution every six months, or sooner if the solution has degraded or evaporated.

7.2.4.5 Calibration Standard Solution

Prepare a calibration standard solution, from the secondary dilution standards, containing all of the purgeable target compounds in methanol. The standard should be prepared at a concentration that can be easily used to prepare the aqueous initial and continuing calibration standards that will bracket the working concentration range. Prepare fresh calibration standard solutions weekly, or sooner if solutions have degraded or evaporated.

7.2.4.6 Initial Calibration Verification (ICV) Standard Solution

Prepare an initial calibration verification standard solution containing all of the purgeable target compounds in methanol, specific for the purge vessel being used, at the concentrations specified below <u>(The ICV standard solution must be prepared from a source/supplier other than that used to prepare the calibration standard solution)</u>:

Compound	ICV Standard Solution (µg/ml) Purge Vessel: 5 ml	25 ml
Acetone, 2-butanone, 2-Hexanone 4-Methyl-2-pentanone	5	25

1,4-Dioxane, Tetrahydrofuran	50	250
All other target and system monitoring compounds	1	5

A 5 µL addition of the appropriate ICV standard solution spiked into the respective volume (5 or 25 ml) of reagent water shall yield a final concentration of 5 µg/L 2-Hexanone, 50 µg/L Tetrahydrofuran, and 1 µg/L of the remaining analytes. Prepare a fresh ICV standard solution weekly, or sooner if the solution has degraded or evaporated.

7.2.4.7 Initial Calibration, Initial Calibration Verification and Continuing Calibration Standards

7.2.4.7.1 Initial Calibration Standards

Use the calibration standard solution (7.2.4.5) to prepare five aqueous initial calibration standard solutions containing all of the purgeable target compounds and system monitoring compounds at the following final concentrations:

Compound	Initial Calibration Range (µg/L)
Acetone, 2-butanone, 2-Hexanone 4-Methyl-2-pentanone	5.0, 10, 25, 50, 125
1,4-Dioxane, Tetrahydrofuran	50, 100, 250, 500, 1250
All other target and system monitoring compounds	2.0, 4.0, 10, 20, 50

7.2.4.7.2 Initial Calibration Verification (ICV) Standard

Use the initial calibration verification standard solution (7.2.4.6) to prepare the aqueous initial calibration verification standard. A 5 µL addition of the appropriate ICV standard solution into the respective volume of reagent water (5 or 25 ml) shall yield a final concentration of each compound at the CRQL.

7.2.4.7.3 Continuing Calibration Standard

The mid-point aqueous initial calibration standard (7.2.4.7.1) is also the continuing calibration standard (e.g. contains 25 µg/L of each of the four ketones, 250 µg/L for 1,4-dioxane and tetrahydrofuran and 10 µg/L of the remaining target and system monitoring compounds).

7.2.4.7.4 Aqueous calibration standards may be prepared in a volumetric flask or in the syringe used to inject the standard into the purging device.

7.2.4.7.4.1 Volumetric flask - add an appropriate volume of the calibration standard solution (Section 7.2.4.5) or initial calibration verification standard solution (Section 7.2.4.6) to an aliquot of reagent water in a volumetric flask. Use a microsyringe and rapidly inject the alcohol standard into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Bring to volume. Mix by inverting the flask three times only. Discard the contents contained in the head of the flask.

7.2.4.7.4.2 Syringe - remove the plunger from a 5 ml (or 25 ml) "Luerlock" syringe. Pour reagent water into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the water. Invert the syringe, open the syringe valve and vent any residual air. Adjust the water volume to 5 ml (or 25 ml) minus the amount of calibration standard to be added. Withdraw the plunger slightly and add an appropriate volume of working calibration standard through the valve bore of the syringe. Close the valve and invert three times.

7.2.4.7.4.3 The methanol contained in each of the aqueous calibration standards must not exceed 1.0 percent by volume.

7.2.5 Ampulated Standard Extracts

Standard solutions purchased from a chemical supply house as ampulated extracts in glass vials may be retained for 2 years from the preparation date, unless the manufacturer recommends a shorter time period. Standard solutions prepared by the Contractor which are immediately ampulated in glass vials may be retained for 2 years from the preparation date. Upon breaking the glass seal, the expiration times listed in Sections 7.2.2 through 7.3 will apply. The Contractor is responsible for assuring that the integrity of the standards has not degraded (see Section 7.3.5).

7.3 Storage of Standard Solutions

7.3.1 Store stock standards in Teflon-sealed screw-cap bottles with zero headspace at -10 °C to -20 °C, and protect the standards from light.

7.3.2 Store secondary dilution standards in Teflon-sealed screw-cap bottles with minimal headspace at -10 °C to -20 °C, and protect the standards from light. The secondary dilution standards must be checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them.

7.3.3 Aqueous standards may be stored for up to 24 hours if held in Teflon-sealed screw-cap vials with zero headspace at 4 °C (±2 °C). Protect the standards from light. If not so stored, they must be discarded after one hour unless they are set up to be purged by an autosampler. When using an autosampler, the standards may be kept for up to 12 hours in purge tubes connected via the autosampler to the purge and trap device. All other non-aqueous working standards must be stored at -10 °C to -20 °C.

7.3.4 Purgeable standards must be stored separately from other standards.

7.3.5 The Contractor is responsible for maintaining the integrity of standard solutions and verifying prior to use. This means that standards must be brought to room temperature prior to use, checked for losses, and checked that all components have remained in the solution.

8.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Sample Collection and Preservation

8.1.1 Water samples are to be collected in duplicate glass containers each having a total volume of at least 40 ml with a Teflon-lined septum and an open top screw-cap. Headspace must be avoided. The specific requirements for site sample collection are outlined by the Region.

8.1.2 For collection of water samples, the container must be filled by the sampler in such a manner that no air bubbles pass through the sample as the container is being filled. The vial is sealed by the sampler so that no air bubbles are entrapped in it. Two vials are filled and submitted for analysis.

8.1.2.1 If one water sample vial has an air bubble and the other does not, then use the other vial for analysis.

8.1.2.2 If both vials have air bubbles, then analyze the sample vial which has fewer and/or smaller air bubbles.

8.1.2.3 If both vials have air bubbles greater than pea-size, then the Contractor shall contact the RSCC to ascertain whether or not the sample should be analyzed.

8.1.2.4 For all samples that contain air bubbles, regardless of size, the Contractor shall note the problem, the EPA sample number for the affected samples and any instructions given by the Region in the SDG Narrative.

8.1.3 Water samples are preserved to a pH of 2 at the time of collection. Water samples not amenable to preservation with acid will not be acidified by the sampler. This fact will be noted on the chain of custody form included with the sample shipment. These unpreserved samples must be analyzed within four days of validated time of sample receipt.

8.1.4 All samples must be iced or refrigerated at 4 °C (±2 °C) from the time of collection until analysis.

8.2 Procedure for Sample Storage

8.2.1 The samples must be protected from light and refrigerated at 4 °C (±2 °C) from the time of receipt until 60 days after delivery of a reconciled, complete sample data package to the Agency. After 60 days, the samples may be disposed of in a manner that complies with all applicable regulations.

8.2.2 If sample storage temperatures exceed 4°C (±2 °C) and/or samples are not light protected, then the Contractor shall contact the RSCC to ascertain whether or not the samples should be analyzed. For all samples that were not properly refrigerated and/or light protected, the Contractor shall note the problem, the EPA sample numbers for the affected samples, and the Region's instructions in the SDG Narrative.

8.2.3 The samples must be stored in an atmosphere demonstrated to be free of all potential contaminants and in a refrigerator used only for storage of volatile samples.

8.2.4 All volatile samples in an SDG must be stored together in the same refrigerator.

8.2.5 Storage blanks shall be stored with the samples contained in an SDG until all samples are analyzed. The storage blank shall be analyzed concurrently with the last sample in the SDG and the results shall be included in the data package per the reporting requirements contained in Exhibit B.

8.2.6 Samples, sample extracts and standards must be stored separately.

8.2.7 Volatile standards must be stored separately from semivolatile and pesticide, Aroclor and herbicide standards.

8.3 Contract Required Holding Times

8.3.1 Analysis of water samples must be completed within 10 days of Validated Time of Sample Receipt (VTSR). As part of the Agency's QA program, the Agency may provide Performance Evaluation samples as standard extracts which the Contractor is required to prepare per the instructions provided by the Agency. The contract required 10 day holding time does not apply to Performance Evaluation Samples received as standard extracts.

8.3.2 If volatile samples have exceeded holding times and have not yet been analyzed, then the Contractor shall contact the RSCC to ascertain whether or not the samples should be analyzed. Note that this notification requirement in no way obviates the contractual requirement for the Contractor to analyze samples within holding times. For all samples that exceeded holding times, the Contractor shall note the problem, the EPA sample numbers for the affected samples, and the Region's instructions in the SDG narrative.

9.0 CALIBRATION AND STANDARDIZATION

9.1 Instrument Operating Conditions

9.1.1 Purge and Trap

9.1.1.1 The following are the recommended purge and trap analytical conditions. The conditions are recommended unless otherwise noted.

Purge Conditions

Purge Gas:	Helium or Nitrogen
Purge Time:	11.0 ± 0.1 minute
Purge Flow Rate:	25-40 ml/minute
Purge Temperature:	Ambient temperature for water

Desorb Conditions

Desorb Temperature:	180 °C
Desorb Flow Rate:	15 ml/minute
Desorb Time:	4.0 ± 0.1 minute

Trap Reconditioning Conditions

Reconditioning Temperature:	180 °C
Reconditioning Time:	7.0 ± 0.1 minute (minimum). A longer time may be required to bake contamination or water from the system.

9.1.1.2 Before initial use, condition the trap overnight at 180 °C by backflushing with at least 20 ml/minute flow of inert gas. Do not vent the trap effluent onto the analytical column. Prior to daily use, condition the trap by heating at 180 °C for 10 minutes while backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to the analysis of samples.

9.1.1.3 Optimize purge and trap conditions for sensitivity and to minimize cross-contamination between samples. Once optimized, the same purge and trap conditions must be used for the analysis of all standards, samples, QC samples and required blanks.

9.1.1.4 A moisture reduction/water management system may be used to improve the chromatographic performance by controlling moisture or water. However the system must meet all method acceptance criteria established in the SOW and Exhibit E.

- The system does not introduce contaminants which interfere with identification and quantitation of compounds listed in Exhibit C (524.2 Volatiles),
- The moisture reduction/water management system must be used for all analyses including the MDL study, initial and continuing calibration, all blank, QC sample and sample analyses. The acceptance criteria established in the SOW and Exhibit E must be achieved for these parameters.

9.1.2 Gas Chromatograph

9.1.2.1 The following are the recommended GC analytical conditions. The conditions are recommended unless otherwise noted.

Packed columns Must not be used for this methodology

Capillary Columns

Carrier Gas:	Helium
Flow Rate:	2-6 ml/minute (column dependent)
Initial Temperature:	10 °C
Initial Hold Time:	1.0 - 5.0 (± 0.1) minutes
Ramp Rate:	6°C/minute
Final Temperature:	160 °C
Final Hold Time:	Until three minutes after all compounds listed in Exhibit C (524.2 Volatiles) elute.

9.1.2.2 Optimize GC conditions for analyte separation and sensitivity. Once optimized, the same GC conditions must be used for the analysis of all standards, samples, QC samples and required blanks.

9.1.2.3 For capillary columns, if the gaseous compounds chloromethane, bromomethane, vinyl chloride, and chloroethane fail to exhibit narrow, symmetrical peak shape, are not separated from the solvent front, or are not resolved greater than 90.0 percent from each other, then a subambient oven controller must be used, and the initial temperature must be less than or equal to 10 °C.

9.1.3 Mass Spectrometer

The following are the required mass spectrometer analytical conditions:

Electron Energy:	70 volts (nominal)
Mass Range:	35-300 amu
Scan Time:	To give at least 5 scans per peak, not to exceed 2 seconds per scan for capillary column.

9.1.4 Purge and Trap Operation

9.1.4.1 Purge and Trap Set Up

9.1.4.1.1 Assemble a purge and trap device that meets the specifications in Section 6.4. Set up and condition the device as described in Section 9.1.1.

9.1.4.1.2 Connect the purge and trap device to the gas chromatograph. The gas chromatograph must be operated using temperature and flow rate parameters equivalent to those established in Section 9.1.2.

9.1.4.1.3 Adjust the purge gas (helium) flow rate to 25-40 ml/minute. Variations from this flow rate may be necessary to achieve better purging and collection efficiencies for some compounds, particularly chloromethane and bromoform.

9.1.4.2 Sample Introduction and Purging

9.1.4.2.1 Remove the plunger from a 5 ml (or 25 ml) syringe and attach a closed syringe valve. Open the aqueous sample or standard bottle which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5 ml (or 25 ml). This process of taking an aliquot destroys the validity of the aqueous sample for future analysis. Thus, if there is only one VOA vial, the analyst must fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time as the analyst has determined that the first sample has been analyzed properly. If an analysis is needed from the second syringe, it must be performed within 24 hours. Care must also be taken to prevent air from leaking into the syringe.

9.1.4.2.2 For standards, add 5 µL of the appropriate internal standard spiking solution (Section 7.2.4.3) through the valve bore of the respective syringe (5 or 25 ml), then close the valve. For samples, add 5 µL of the appropriate system monitoring compound spiking solution (Section 7.2.4.1) and 5 µL of the appropriate internal standard spiking solution (Section 7.2.4.3) through the valve bore of the respective syringe (5 or 25 ml), then close the valve. The addition of 5 µL of the system monitoring compound and/or 5 µl of internal standard spiking solution to the sample or standard is equivalent to a final concentration of 2 µg/L of each system monitoring compound and each internal standard. NOTE: The system monitoring compound and internal standard compound solutions are not added to the GC/MS instrument performance check solution. The system monitoring compounds and internal standards may be mixed and added as a single spiking solution.

9.1.4.2.3 Attach the syringe valve of the syringe to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

9.1.4.2.4 Close both valves and purge the sample for 11.0 ± 0.1 minutes at ambient temperature.

9.1.4.3 Sample Desorption

9.1.4.3.1 At the conclusion of the purge time, transfer the trapped volatile organics to the gas chromatograph. Concurrently, switch the purge and trap to the desorb mode, rapidly heat the trap to 180°C, and then backflush the trap with helium gas (at 25 to 40 ml/minute) for 4 minutes into the GC inlet.

9.1.4.3.2 While the trap is being desorbed into the gas chromatograph, empty the purging chamber. Wash the chamber with a minimum of two 5 ml (or 25 ml) flushes of reagent water to avoid carryover of target compounds. It may be necessary to wash out the purging device with a detergent solution, rinse it with distilled water, and then dry it in an oven at 105°C between analyses.

9.1.4.4 Trap Reconditioning

9.1.4.4.1 After desorbing the sample for four minutes, recondition the trap by returning the purge and trap device to the purge mode. Wait 15 seconds, then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 180 °C. Trap temperatures up to 220 °C may be employed. However, the higher temperature will shorten the useful life of the trap. After approximately seven minutes, turn off the trap heater and return to the standby mode. When cool, the trap is ready for the next sample.

9.2 GC/MS Calibration (Tuning) and Ion Abundance

9.2.1 Summary of GC/MS Instrument Performance Check

9.2.1.1 The Mass Spectrometer must be initially tuned to meet the manufacturer's specifications, using a suitable calibrant such as perfluoro-tri-n-butylamine (PFTBA) or perfluorokerosene (PFK).

9.2.1.2 The mass calibration and resolution of the GC/MS system are verified by the analysis of the instrument performance check solution (Section 7.2.4.4). Prior to the analysis of any samples, including QC samples, blanks, or calibration standards, the Contractor must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check solution containing BFB.

9.2.1.3 If the technical acceptance criteria for GC/MS Instrument Performance Checks are not met, then the contractor must stop and correct the problem before continuing the analytical sequence.

9.2.2 Frequency of GC/MS Instrument Performance Check

The instrument performance check solution must be injected once at the beginning of each 12-hour period, during which samples or standards are to be analyzed. The twelve (12) hour time period for GC/MS instrument performance check (BFB), standards calibration (initial or continuing calibration criteria), blank, sample and QC sample analysis begins at the moment of injection of the BFB analysis that the laboratory submits as documentation of a compliant instrument performance check. The time period ends after twelve (12) hours have elapsed according to the system clock.

9.2.3 Procedure for GC/MS Instrument Performance Check

9.2.3.1 The analysis of the instrument performance check solution may be performed as follows:

- As an injection of up to 25 ng of BFB into the GC/MS.
- By adding 25 ng of BFB to 5 ml (or 25 ml) of reagent water and analyzing the resulting solution as if it were a sample (see Section 9.1.4). NOTE: Internal standard or system monitoring compound solutions are not added to the BFB analysis.

9.2.3.2 The GC/MS instrument performance check solution must be analyzed alone without calibration standards. BFB key ion abundances are compared to established ion abundance criteria for BFB outlined in Table 1.

9.2.4 Technical Acceptance Criteria for GC/MS Instrument Performance Check

9.2.4.1 The mass spectrum of BFB must be acquired in the following manner. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan no more than 20 scans prior to the elution of BFB. Do not background subtract part of the BFB peak.

9.2.4.2 All subsequent standards, samples, QC samples, and blanks associated with a BFB analysis must use identical mass spectrometer instrument conditions.

9.2.4.3 The analysis of the GC/MS instrument performance check solution must meet the ion abundance criteria given in Table 1.

9.2.5 Corrective Action for GC/MS Instrument Performance Check

9.2.5.1 If the GC/MS instrument performance check technical acceptance criteria are not met, retune the GC/MS system (Section 9.2.1). If the GC/MS system cannot be retuned, then it may be necessary to clean the ion source, clean the quadrupole rods, or take other corrective actions to achieve the technical acceptance criteria.

9.2.5.2 GC/MS instrument performance check technical acceptance criteria **must** be met before any standards, samples, including QC samples or required blanks are analyzed. Any samples, QC samples or required blanks analyzed when GC/MS instrument performance check technical acceptance criteria have not been met will require reanalysis at no additional cost to the Agency. Reanalyses must be performed within contract required holding times and must meet all technical acceptance criteria.

9.2.5.3 Sample analyses reported with a non-compliant GC/MS Instrument Performance Check shall receive a commensurate reduction in sample price or zero payment due to data rejection depending upon the impact of the non-compliance on data usability.

9.3 Initial Calibration

9.3.1 Summary of Initial Calibration

9.3.1.1 Prior to the analysis of samples, QC samples, required blanks, and after the instrument performance check solution criteria have been met, each GC/MS system must be calibrated at five concentrations to determine instrument sensitivity and the linearity of GC/MS response for the purgeable target compounds.

9.3.1.2 If the technical acceptance criteria for initial calibration are not met, then the Contractor must stop and correct the problem before continuing the analytical sequence.

9.3.2 Frequency of Initial Calibration

9.3.2.1 Each GC/MS system must be calibrated upon award of the contract, whenever the Contractor takes corrective action which may change or affect the initial calibration criteria (e.g., ion source cleaning or repair, column replacement, etc.), or if the continuing calibration technical acceptance criteria have not been met.

9.3.2.2 If time remains in the 12-hour time period after meeting the technical acceptance criteria for the GC/MS instrument performance check and initial calibration, samples may be analyzed. It is not necessary to analyze a continuing calibration standard if the initial calibration standard that is the same concentration as the continuing calibration standard meets the continuing calibration technical acceptance criteria. A method blank is required. Quantify all sample and quality control sample results, such as internal standard area response change and retention time shift, against the initial calibration standard that is the same concentration as the continuing calibration standard.

9.3.3 Procedure for Initial Calibration

9.3.3.1 Add 5 µl of the appropriate amount of the internal standard solution (Section 7.2.4.3) to each of the five aqueous calibration standard solutions containing the system monitoring compounds (Section 7.2.4.7.1) for a concentration of 2 µg/L at time of purge. Analyze each calibration standard according to Section 9.1.4.

9.3.4 Calculations for Initial Calibration

9.3.4.1 Calculate the relative response factor (RRF) for each volatile target and system monitoring compound using equation 1. The primary characteristic ions used for quantitation of target compounds, system monitoring compounds and internal standards are listed in Table 2 and Table 4. Assign the target compounds and system monitoring compounds to an internal standard according to Table 3. If an interference prevents the use of a primary ion for a given internal standard, use a secondary ion listed in Table 4. NOTE: Unless otherwise stated, the area response of the primary characteristic ion is the quantitation ion. If interference in a sample requires a secondary ion to be used for quantitation, then the initial and continuing calibration standards must also be calculated using the secondary ion.

EQ. 1

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$

Where,

A_x = Area of the characteristic ion (EICP) for the compound to be measured (see Table 2)
A_{is} = Area of the characteristic ion (EICP) for the specific internal standard (see Tables 3 and 4)
C_{is} = Concentration of the internal standard
C_x = Concentration of the compound to be measured

9.3.4.2 Calculating the relative response factor (RRF) of the xylenes requires special attention. On capillary columns, the m-xylene and p-xylene isomers coelute. Therefore, quantitation of total xylenes shall be based on the RRF for o-xylene which does not coelute.

9.3.4.3 All other isomeric compounds such as cis/trans-1,2-dichloroethene and the dichlorobenzenes must be resolved chromatographically and reported as separate compounds with unique RRFs.

9.3.4.4 Calculate the mean relative response factor for all compounds using equation 2.

EQ. 2

$$\overline{RRF} = \frac{\sum_{i=1}^{n} RF_i}{n}$$

Where,

RF_i = each individual value used to calculate the mean
$\overline{RRF}$ = the mean RRF
n = the total number of values

9.3.4.5 Calculate the % Relative Standard Deviation (%RSD) of the RRF values over the working range of the curve using equation 3.

EQ. 3

$$\%RSD = \frac{Standard\ Deviation}{\overline{RRF}} \times 100$$

Where

$$Standard\ Deviation = \sqrt{\frac{\sum_{i=1}^{n} (RF_i - \overline{RRF})^2}{(n-1)}}$$

9.3.5 Technical Acceptance Criteria for Initial Calibration

9.3.5.1 All initial calibration standards must be analyzed at the concentration levels described in Section 7.2.4.7.1, and at the frequency described in Section 9.3.2 on a GC/MS system meeting the GC/MS instrument performance check technical acceptance criteria.

9.3.5.2 The relative response factor (RRF) at each calibration concentration for each purgeable target and system monitoring compound must be greater than or equal to the compound's minimum acceptable response factor listed in Table 5.

9.3.5.3 The %RSD for each target or system monitoring compound must be less than or equal to the compound's maximum acceptable %RSD listed in table 5.

9.3.5.4 Up to two compounds may fall outside the criteria listed in Sections 9.3.5.2 and 9.3.5.3 and still meet the minimum response factor and %RSD requirements. However, these compounds must have a minimum RRF greater than or equal to 0.010, and the %RSD must be less than or equal to 40.0 percent.

9.3.5.5. Excluding those ions in the solvent front and the combined xylenes, no quantitation ion may saturate the detector. Follow the manufacturer's instrument operating manual to determine how saturation is indicated for your instrument.

9.3.6 Corrective Action for Initial Calibration

9.3.6.1 If the initial calibration technical acceptance criteria are not met, inspect the entire analytical system for problems. It may be necessary to clean the ion source, change the column, service the purge and trap device or take other corrective actions to achieve the technical acceptance criteria.

9.3.6.2 Initial calibration technical acceptance criteria **must** be met before any samples, QC samples or required blanks are analyzed. Any samples, QC samples or required blanks analyzed when initial calibration technical acceptance criteria have not been met will require reanalysis at no additional cost to the Agency. Reanalyses must be performed within contract required holding times and must meet all sample technical acceptance criteria.

9.3.6.3 Sample results reported with a non-compliant initial calibration after reanalysis shall receive a commensurate reduction in sample price or zero payment due to data rejection depending upon the impact of the non-compliance on data usability.

9.4 Initial Calibration Verification

9.4.1 Summary of Initial Calibration Verification

9.4.1.1 Prior to the analysis of samples, QC samples, required blanks and after the GC/MS instrument performance check solution criteria and initial calibration technical criteria have been met, the initial calibration must be verified with a separate source standard.

9.4.1.2 If the technical acceptance criteria for the initial calibration verification are not met, then the Contractor must stop and correct the problem before continuing the analytical sequence.

9.4.2 Frequency of Initial Calibration Verification

A second source verification of the initial calibration curve must be performed by the Contractor upon award of the contract, whenever an initial calibration is performed and whenever the Contractor takes corrective action which may change or affect the initial calibration criteria (e.g., ion source cleaning or repair, column replacement, etc.).

9.4.3 Procedure for Initial Calibration Verification

9.4.3.1 Analyze the initial calibration verification standard prepared in Section 7.2.4.7.2 following the sample analysis procedure in Section 9.1.4.

9.4.3.2 The initial calibration verification standard must be analyzed using the same analytical conditions established for the initial calibration.

9.4.4 Calculations for Initial Calibration Verification

9.4.4.1 Calculate the relative response factor (RRF) for each volatile target and system monitoring compound using Equation 1.

9.4.4.2 Calculate the percent difference between the initial calibration verification standard relative response factor and the most recent initial calibration mean relative response factor for each purgeable target and system monitoring compound using Equation 4.

EQ. 4

$$\%Difference = \frac{RRF_c - \overline{RRF_i}}{\overline{RRF_i}} \times 100$$

Where,

RRF_c = Relative response factor from initial calibration verification standard

RRF_i = Mean relative response factor from the most recent initial calibration meeting technical acceptance criteria

Note: The initial calibration verification results must be reported on an appropriate form and must be included in the data package with the associated initial calibration data.

9.4.5 Technical Acceptance Criteria for the Initial Calibration Verification

9.4.5.1 The initial calibration verification standard must be analyzed at the concentration level described in Section 7.2.4.7.2, and at the frequency described in Section 9.4.2 on a GC/MS system meeting the GC/MS Instrument Performance check and initial calibration technical acceptance criteria.

9.4.5.2 The relative response factor (RRF) for each purgeable target and system monitoring compound must be greater than or equal to the compounds's minimum acceptable response factor listed in Table 5.

9.4.5.3 The relative response factor percent difference for each purgeable target and system monitoring compound must be less than or equal to ± 30.0 percent.

9.4.5.4 Up to two compounds may fail the requirements listed in Sections 9.4.5.2 and 9.4.5.3 and still meet the minimum relative response factor criteria and percent difference criteria. However, these compounds must have a minimum relative response factor greater than or equal to 0.010 and the percent difference must be within the inclusive range of ± 40.0 percent.

9.4.6 Corrective Action for Initial Calibration Verification

9.4.6.1 If the initial calibration verification technical acceptance criteria are not met, reanalyze and check the initial calibration verification standard following Sections 9.4.3 and 9.4.4. If the reanalysis meets the technical acceptance criteria established in Section 9.4.5, then proceed with sample analysis.

9.4.6.2 If the reanalysis still does not meet the technical acceptance criteria, examine the preparation procedures and calculations which were used to make the initial calibration and initial calibration verification solutions. If the procedures or calculations were incorrect, correct the calculations and verify the technical acceptance criteria. It may be necessary to take other corrective actions to achieve the initial calibration technical acceptance criteria.

9.4.6.3 Initial calibration verification technical acceptance criteria **must** be met before any samples, QC samples, or required blanks are analyzed. Any samples, QC sample, required blanks or continuing calibrations analyzed when the initial calibration verification technical acceptance criteria have not been met must be reanalyzed at no additional cost to the Agency. Reanalyses must be performed within contract required holding times and must meet all sample technical acceptance criteria.

9.4.6.4 Sample results reported with a non-compliant initial calibration verification standard after reanalysis shall receive a commensurate reduction in sample price or zero payment due to data rejection depending upon the impact of the non-compliance on data usability.

9.5 Continuing Calibration

9.5.1 Summary of Continuing Calibration

Prior to the analysis of samples, QC samples and required blanks and after the GC/MS instrument performance check, initial calibration and initial calibration verification technical acceptance criteria have been met, each GC/MS system must be routinely checked by analyzing a continuing calibration standard, containing all the purgeable target and system monitoring compounds, to ensure that the instrument continues to meet the sensitivity and stability requirements of the SOW.

9.5.2 Frequency of Continuing Calibration

9.5.2.1 A check of the calibration curve must be performed once every 12 hours (see Section 9.2.2 for the definition of the 12-hour time period). If time remains in the 12-hour time period after meeting the technical acceptance criteria for the initial calibration and initial calibration verification, samples may be analyzed. It is not necessary to analyze a continuing calibration standard if the initial calibration standard that is the same concentration as the continuing calibration standard meets the continuing calibration technical acceptance criteria. A method blank is required. Quantify all sample results against the initial calibration standard that is the same concentration as the continuing calibration standard (Section 7.2.4.7.3).

9.5.2.2 If time does **not** remain in the 12-hour period beginning with the injection of the GC/MS instrument performance check, a new injection of the GC/MS instrument performance check must be made. If the new injection meets the ion abundance criteria for BFB, then a continuing calibration standard may be injected.

9.5.3 Procedure for Continuing Calibration

9.5.3.1 Set up the purge and trap GC/MS system per the requirements in Section 9.1.

9.5.3.2 Add 5 µl of the appropriate internal standard spiking solution (Section 7.2.4.3) to the 5 ml (or 25 ml) syringe or volumetric flask containing the continuing calibration standard (Section 7.2.4.7.3). Analyze the continuing calibration standard according to Section 9.1.4.

9.5.4 Calculations for Continuing Calibration

9.5.4.1 Calculate a relative response factor (RRF) for each target and system monitoring compound using Equation 1.

9.5.4.2 Calculate the percent difference between the continuing calibration relative response factor and the most recent initial calibration mean relative response factor for each purgeable target and system monitoring compound using Equation 4.

9.5.5 Technical Acceptance Criteria for Continuing Calibration

9.5.5.1 The continuing calibration standard must be analyzed at the frequency described in Section 9.4.2 on a GC/MS system meeting the GC/MS instrument performance check, initial calibration and initial calibration verification technical acceptance criteria.

9.5.5.2 The relative response factor (RRF) for each purgeable target and system monitoring compound must be greater than or equal to the compound's minimum acceptable response factor listed in Table 5.

9.5.5.3 The relative response factor percent difference (%D) for each purgeable target and system monitoring compound must be less than or equal to the compound's maximum acceptable %D listed in Table 5.

9.5.5.4 Up to two compounds may fail the requirements listed in Sections 9.4.5.2 and 9.4.5.3 and still meet the minimum relative response factor criteria and percent difference criteria. However, these compounds must have a minimum relative response factor greater than or equal to 0.010 and the percent difference must be within the inclusive range of ±40.0 percent.

9.5.5.5 Excluding those ions in the solvent front, no quantitation ion may saturate the detector. Consult the manufacturer's instrument operating manual to determine how saturation is indicated for your instrument.

9.5.6 Corrective Action for Continuing Calibration

9.5.6.1 If the continuing calibration technical acceptance criteria are not met, recalibrate the GC/MS instrument according to Section 9.3.3. It may be necessary to clean the ion source, change the column or take other corrective actions to achieve the continuing calibration technical acceptance criteria.

9.5.6.2 Continuing calibration technical acceptance criteria **must** be met before any samples, QC samples or required blanks are analyzed. Any samples, QC samples or required blanks analyzed when continuing calibration technical acceptance criteria have not been met will require reanalysis at no additional cost to the Agency. Reanalyses must be performed within contract required holding times and must meet all sample technical acceptance criteria.

9.5.6.3 Sample analyses reported with a non-compliant continuing calibration after reanalysis shall receive a commensurate reduction in sample price or zero payment due to data rejection depending upon the impact of the non-compliance on data usability.

10.0 PROCEDURE

10.1 Sample Preparation

10.1.1 If insufficient sample volume (less than 90% of the required volume) is received to perform the analyses, the Contractor shall contact the RSCC for instructions. The Region will either require that no sample analyses be performed or will require that a reduced volume be used for the sample analysis. Changes in the sample analysis must be preapproved by the Region. The Contractor shall document the problem, the EPA sample numbers for the affected samples, and the Region's instructions (including sample volume prepared and analyzed) in the SDG Narrative.

10.1.2 Water Samples

10.1.2.1 pH Determination (Water Samples)

Once the sample aliquots have been taken from the VOA vial, the pH of the aqueous sample must be determined. The purpose of the pH determination is to ensure that all volatile samples were acidified in the field. Test the pH by placing one or two drops of sample on the pH paper (do **not** add pH paper to the vial). Record the pH of each sample and report on the Form I.

10.1.2.2 All water samples must be allowed to warm to ambient temperature before analysis.

10.1.2.3 Prior to the analysis of samples, establish the appropriate purge and trap GC/MS operating conditions, as outlined in Section 9.1, analyze the GC/MS instrument performance check solution (9.2), and calibrate the GC/MS system according to Sections 9.3 through 9.5.6. These procedures should coincide with the completion of sample preparation to avoid loss of volatiles from standards and samples.

10.1.2.4 If time remains in the 12-hour period (as described in Section 9.3.2), samples may be analyzed without analysis of a continuing calibration standard.

10.1.2.5 If time does **not** remain in the 12-hour period since the injection of the GC/MS instrument performance check solution, both the GC/MS instrument performance check solution and the continuing calibration standard must be reanalyzed and must meet technical acceptance criteria before sample analysis may begin.

10.1.2.6 Prior to sample analysis and after calibration technical acceptance criteria have been met, the GC/MS system must be demonstrated to be free of contamination by the analysis of instrument and method blanks as specified in Section 12.1.2 and 12.1.3. All technical acceptance criteria for blank analyses defined in Section 12.1.4 must be met before proceeding with sample analyses.

10.1.2.7 Analyze a 5 ml (or 25 ml) aliquot of the aqueous sample according to Section 9.1.4.

10.1.2.8 Proceed with Data Analysis and Calculations as described in Section 11.0. All technical acceptance criteria (Section 11.4) must be met before sample results are reported.

10.1.3 Sample Dilutions

10.1.3.1 If the on-column concentration of any compound in any sample exceeds the initial calibration range, a new aliquot of that sample must be diluted and purged. Guidance in performing dilutions and exceptions to this requirement are given in Sections 10.1.3.2 through 10.1.3.7.

10.1.3.2 Use the results of the original analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range.

10.1.3.3 The dilution factor chosen should keep the response of the largest analyte peak for a target compound in the upper half of the initial calibration range of the instrument.

10.1.3.4 Dilutions for water samples may be performed in volumetric flasks (10 ml to 100 ml).

10.1.3.5 Volumetric Dilutions

10.1.3.5.1 Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for extremely large dilutions. However, the Contractor must make every effort to minimize the number of dilutions in order to minimize potential dilution errors.

10.1.3.5.2 Calculate the approximate volume of reagent water which will be added to the volumetric flask selected and add slightly less than this quantity of reagent water to the flask.

10.1.3.5.3 For water samples, inject the proper aliquot from the syringe prepared in Section 9.1.4.2.1 into the volumetric flask. Aliquots of less than 1 ml increments are prohibited. Dilute the flask to the mark with reagent water. Cap the flask, invert, and shake three times.

10.1.3.5.4 Fill a 5 ml syringe with the diluted sample as in Section 9.1.4.2.1. If this is an intermediate dilution, use it and repeat the above procedure to achieve larger dilutions.

10.1.3.5.5 After the sample dilution is complete, proceed with sample analysis in Section 9.1.4.2.2.

10.1.3.6 Do **not** submit data for more than two analyses, i.e., the original sample and **one** dilution, or, from the most concentrated dilution analyzed and one further dilution.

10.1.3.7 For total xylenes, where three isomers are quantified as two peaks, the calibration of each peak should be considered separately, i.e., a diluted analysis is **not** required for total xylenes unless the concentration of the peak representing the single isomer exceeds 50 µg/L or the peak representing the two co-eluting isomers on the GC column exceeds 100 µg/L. All other isomers must be chromatographically separated. Therefore, each isomeric peak must not exceed the upper limit of the initial calibration range.

10.1.3.8 The Contractor may receive instructions with the sampling paperwork which prohibits sample dilutions under any circumstances. This may be required in instances where the CRQLs for most target compounds must be achieved even though one or more target compounds exceed the calibration range and/or high concentrations of non-target compounds are present. In these cases, if screening results indicate that sample dilution is required to avoid detector saturation due to target and/or non-target compound ions, then the contractor shall contact the RSCC to ascertain whether or not that sample should be analyzed at a dilution. For all samples affected by this situation, the Contractor shall note the problem, the EPA sample numbers affected by this situation, and the Regional instructions in the SDG Narrative.

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Qualitative Identification

11.1.1 Identification of Target Compounds

11.1.1.1 The compounds listed in the Target Compound List (TCL) in Exhibit C (524.2 Volatiles) shall be identified by an analyst competent in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. Two criteria must be satisfied to verify the identifications: (1) elution of the sample component at the same GC relative retention time as the standard component, and (2) correspondence of the sample component and standard component mass spectra.

11.1.1.2 For establishing correspondence of the GC relative retention time (RRT), the sample component RRT must compare within ±0.06 RRT units of the RRT of the standard component. For reference, the standard must be run in the same 12-hour time period as the sample. If samples are analyzed during the same 12-hour time period as the initial calibration standards, use the RRT values from the mid point (10 µg/L) standard. If co-elution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

11.1.1.3 For comparison of standard and sample component mass spectra, mass spectra obtained on the Contractor's GC/MS are required. Once obtained, these standard spectra may be used for identification purposes, **only** if the Contractor's GC/MS meets the daily GC/MS instrument performance check technical acceptance criteria. These standard spectra may be obtained from the run used to obtain reference RRTs.

11.1.1.4 The requirements for qualitative verification by comparison of mass spectra are as follows:

- All ions present in the standard mass spectra at a relative intensity greater than 10.0 percent (most abundant ion in the spectrum equals 100.0 percent) **must** be present in the sample spectrum.
- The relative intensities of ions specified above must agree within ± 20.0 percent between the standard and sample spectra. (Example: For an ion with an abundance of 50.0 percent in the standard spectra, the corresponding sample abundance must be between 30.0 and 70.0 percent).
- Ions greater than 10.0 percent in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. All compounds meeting the identification criteria must be reported with their spectra. For all compounds with positive matches that are detected below the CRQL, report the actual value followed by a "J", e.g., "3J".

11.1.1.5 If a compound cannot be verified by all of the criteria in 11.1.1.4, but in the technical judgment of the mass spectral interpretation specialist, the identification is correct, then the Contractor shall report that identification on Form I qualified with an "X". The Contractor must note this decision in the SDG Narrative and proceed with quantitation as described in Section 11.2.

11.1.2 Identification of Non-Target Compounds

11.1.2.1 A library search shall be executed for non-target sample components for the purpose of tentative identification. The NIST/EPA/NIH (May 1992 release or the most recent release) and/or Wiley (1991 release or the most recent release), or equivalent mass spectral library, shall be used.

11.1.2.2 Up to 10 organic compounds of greatest apparent concentration not listed in Exhibit C for the low concentration volatile fraction, excluding the system monitoring compounds, and internal standard compounds, shall be identified tentatively via a forward search of the NIST/EPA/NIH (May 1992 release or the most recent release) and/or Wiley (1991 release or the most recent release), or equivalent mass spectral library. The following are not to be reported: 1) Substances with responses less than 10 percent of the nearest internal standard free of interferences (as determined by inspection of the peak areas or height), 2) Substances which elute earlier than 30 seconds before the first purgeable compound listed in Exhibit C (524.2 Volatiles) or three minutes after elution of the last purgeable compound listed in Exhibit C (524.2 Volatiles) are not required to be searched in this fashion, and 3) Carbon dioxide. The mass spectral interpretation specialist will assign a tentative identification only after visual comparison of the sample spectrum with all the library search spectra.

11.1.2.3 NOTE: Computer generated library search routines must not use normalizations which would misrepresent the library or unknown spectra when compared to each other.

11.1.2.4 Guidelines for making tentative identification:

- Relative intensities of major ions in the reference spectrum (ions greater than 10.0 percent of the most abundant ion) should be present in the sample spectrum.
- The relative intensities of the major ions should agree within ±20.0 percent of the reference and sample spectra. (Example: For an ion with an abundance of 50.0 percent of the reference spectra, the corresponding sample ion abundance must be between 30.0 and 70.0 percent.)
- Molecular ions present in reference spectrum should be present in sample spectrum.
- Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.
- Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting compounds. Data system library reduction programs can sometimes create these discrepancies.

11.1.2.5 If, in the technical judgment of the mass spectral interpretation specialist, no valid tentative identification can be made, then the compound should be reported as **unknown**. The mass spectral interpretation specialist should give additional classification of the unknown compound, if possible (i.e., unknown aromatic, unknown hydrocarbon, unknown acid type, unknown chlorinated compound). If probable molecular weights can be distinguished, then the mass spectral interpretation specialist should include them on the Form I 524.2-TIC and provide discussion in the SDG Narrative.

11.2 Calculations

11.2.1 Target Compounds

11.2.1.1 Target compounds which meet the identification criteria in Section 11.1, shall be quantified by the internal standard method using the equations below. The internal standard used shall be that which is assigned in Table 3. The relative response factor (RRF) from the continuing calibration standard shall be used to calculate the concentration of that target compound in the sample.

11.2.1.2 Water

EQ. 5

$$Concentration\ \mu g/L = \frac{(A_x)(I_s)(Df)}{(A_{is})(RRF)(V_o)}$$

Where,

A_x = Area of the characteristic ion (EICP) for the compound to be measured (see Table 2)
A_{is} = Area of the characteristic ion (EICP) for the specific internal standard (see Tables 3 and 4)
I_s = Amount of internal standard added in nanograms (ng)
RRF = Relative response factor from the purge of the calibration standard.
V_o = Volume of water purged in milliliters (ml)
Df = Dilution factor. The dilution factor for analysis of water samples for volatiles by this method is defined as the ratio of the number of milliliters (ml) of water purged (i.e., V_o above) to the number of ml of the original water sample used for purging. For example, if 2.0 ml of sample is diluted to 5 ml with reagent water and purged, Df = 5 ml/2.0 ml = 2.5. If no dilution is performed, Df = 1.

11.2.1.3 Xylenes (o-,m- and p-isomers) are to be reported as xylenes (total). Because the – and p-xylene isomers co-elute on capillary columns, special attention must be given to the quantitation of the xylenes. The relative response factor (RRF) determined in Section 9.5.4 is based on the peak that represents the single isomer on the GC column used, o-xylene on capillary columns. In quantitating sample concentrations, use the areas on both peaks and the RRF from Section 9.5.4. The areas of the two peaks may be summed, and the concentration determined, or the concentration represented by each of the two peaks may be determined separately, and then summed. It is required that all three xylene isomers be present in the initial and continuing calibration standards.

11.2.1.4 All other isomers must be chromatographically separated. Relative response factors must be determined for each isomer.

11.2.1.5 Secondary ion quantitation is allowed **only** when there are sample matrix interferences with the primary ion. If secondary ion quantitation is performed, document the reasons and the EPA sample numbers in the SDG Narrative. A secondary ion cannot be used unless a relative response factor is calculated using the secondary ion.

11.2.1.6 The requirements listed in 11.2.1.7 and 11.2.1.8 apply to all standards, samples, QC samples, and blanks.

11.2.1.7 It is expected that situations will arise where the automated quantitation procedures in the GC/MS software provide inappropriate quantitations. This normally occurs when there is compound co-elution, baseline noise, or matrix interferences. In these circumstances the Contractor must perform a manual quantitation. Manual quantitations are performed by integrating the area of the quantitation ion of the compound. This integration shall only include the area attributable to the specific TCL compound. The area integrated shall not include baseline background noise. The area integrated shall not extend past the point where the sides of the peak intersect with the baseline noise. Manual integration is not to be used solely to meet QC criteria, nor is it to be used as a substitute for corrective action on the chromatographic system. Any instances of manual integration, along with the EPA sample numbers, must be documented in the SDG Narrative.

11.2.1.8 In all instances where the data system report has been edited, or where manual integration or quantitation has been performed, the GC/MS operator must identify such edits or manual procedures by initialing and dating the changes made to the report, and the

GC/MS operator must include the integration scan range on the report. In addition, a hardcopy printout of the EICP of the quantitation ion displaying the manual integration shall be included in the raw data. This applies to all compounds listed in Exhibit C (524.2 Volatiles), internal standards and system monitoring compounds.

11.2.2 Non-Target Compounds

11.2.2.1 An estimated concentration for non-target compounds tentatively identified shall be determined by the internal standard method. For quantitation, the nearest internal standard free of interferences shall be used.

11.2.2.2 The formula for calculating concentration is the same as in Sections 11.2.1.2. Total area counts (or peak heights) from the total ion chromatograms are to be used for both the compound to be measured and the internal standard. A relative response factor (RRF) of one (1) is to be assumed. The resulting concentration shall be qualified as "J" (estimated, due to lack of a compound-specific response factor), and "N" (presumptive evidence of presence), indicating the quantitative and qualitative uncertainties associated with this non-target component. An estimated concentration must be calculated for all tentatively identified compounds as well as those identified as unknowns.

11.2.3 CRQL Calculations

Sample specific CRQLs must be calculated and reported on Form I. If the adjusted CRQL is less than the CRQL listed in Exhibit C (524.2 Volatiles), report the CRQL listed in Exhibit C. If the adjusted CRQL is greater than the CRQL listed in Exhibit C (524.2 Volatiles), report the adjusted CRQL.

11.2.3.1 Water

EQ. 6

$$\underset{CRQL}{Adjusted} = \underset{CRQL}{Contract} \times \frac{V_x}{V_o} \times Df$$

Where,

V_o and Df are as given in Equation 5
V_x = Contract Sample Volume (5 ml or 25 ml)

11.2.4 System Monitoring Compound Recoveries

11.2.4.1 Calculate the concentrations of the system monitoring compounds for all samples, QC samples and required blanks using equation 5.

11.2.4.2 Calculate the recovery of each system monitoring compound in all samples, QC samples, or required blanks using equation 7 below. Determine if the recoveries are within the technical acceptance criteria listed in Table 7, and report on Form II as specified in Exhibit B.

EQ. 7

$$\%Recovery = \frac{Concentration\ (amount)\ found}{Concentration\ (amount)\ spiked} \times 100$$

11.2.5 Internal Standard Responses and Retention Times

Internal standard responses and retention times in all samples, QC samples and required blanks must be evaluated during or immediately after data acquisition. Compare the sample internal standard responses and retention times to the continuing calibration internal standard response and retention times. For samples analyzed during the same 12-hour time period as the initial calibration standards, compare the internal standard responses and retention times against the 10 µg/ml calibration standard. The extracted ion current profile (EICP) of the internal standards must be monitored and evaluated for each sample, QC sample and required blank.

11.3 Technical Acceptance Criteria for Sample Analysis

Target and non target compounds in samples are identified and reported following procedures defined in Sections 11.1 and 11.2. Sample analysis technical acceptance criteria must be met before any sample data can be reported.

11.3.1 The samples must be analyzed on a GC/MS system meeting the GC/MS instrument performance check, initial calibration, initial calibration verification, and continuing calibration technical acceptance criteria defined in Sections 9.2.5, 9.3.5, 9.4.5 and 9.5.5, respectively.

11.3.2 The sample must be analyzed, or reanalyzed, within the contract required holding times defined in Section 8.3.

11.3.3 The sample must have associated method, storage and instrument blank meeting the blanks meeting the blank technical acceptance criteria defined in Section 12.1.4.

11.3.4 The percent recovery of each of the system monitoring compounds in the sample must be within the technical acceptance windows listed in Table 6.

11.3.5 The EICP area (or height) response for each of the internal standards must be within the inclusive range of -50.0 percent and +100.0 percent of the response of the internal standards in the most recent continuing calibration analysis (or the 10 µg/L initial calibration standard, if appropriate).

11.3.6 The retention time shift for each of the internal standards must be within ± 0.50 minutes (30 seconds) between the sample internal standard retention time and the most recent continuing calibration standard (or the 10 µg/L initial calibration standard, if appropriate) internal standard retention times.

11.3.7 The relative retention time (RRT) of the system monitoring compound in a sample must be within ±0.06 (RRT) units of its relative retention time in the continuing calibration standard (or the 10 µg/L initial calibration standard, if appropriate).

11.3.8 Excluding those ions in the solvent front, no ion from a target or non-target compound may saturate the detector. No target compound concentration may exceed the upper limit of the initial calibration range unless a more diluted aliquot of the sample is also analyzed according to the procedures in Section 10.1.3.

11.3.9 The Contractor must demonstrate that there is no carryover from a contaminated sample before data from subsequent analyses may be submitted. After a sample that contains a target compound at a level exceeding the initial calibration range, the Contractor must either:

- Analyze an instrument blank immediately after the contaminated sample. If an autosampler is used, an instrument blank must also be analyzed using the same purge inlet that was used for the contaminated sample. The instrument blanks must meet the technical acceptance criteria for blank analysis (see Section 12.1.4), or

- Monitor the sample analyzed immediately after the contaminated sample for all compounds that were in the contaminated sample and that exceeded the calibration range. The maximum contamination criteria are as follows: the sample must not contain a concentration above the CRQL for the target compounds that exceeded the limits in the contaminated sample. If an auto sampler is used, the next sample analyzed using the same purge inlet that was used for the contaminated sample also must meet the maximum contamination criteria. If the maximum criteria were exceeded, then all samples affected by the carryover must be reanalyzed at no additional cost to the Agency.

11.4 Corrective Action for Sample Analysis

11.4.1 Sample technical acceptance criteria <u>must</u> be met before data are reported. Samples contaminated from laboratory sources or sample results which failed to meet the sample technical acceptance criteria require reanalysis at no additional cost to the Agency.

11.4.2 Corrective actions for failure to meet GC/MS instrument performance checks, initial calibration, initial calibration verification and continuing calibration must be completed before the analysis of samples.

11.4.3 Corrective actions for failure to meet all blank technical acceptance criteria must be completed before the analysis of samples.

11.4.3 Corrective actions for system monitoring compound recoveries and/or internal standard compound responses that fail to meet technical acceptance criteria are defined below.

11.4.3.1 If any of the system monitoring compound recoveries and/or internal standard compound responses fail to meet acceptance criteria:

- Check all calculations, instrument logs, the system monitoring compound and internal standard compound spiking solutions, and the instrument operation. If the calculations were incorrect, correct the calculations and verify that the system monitoring compound recoveries and internal standard compound responses meet technical acceptance criteria.

- If the instrument logs indicate that the incorrect amount of system monitoring compound or internal standard compound spiking solution was added, then reanalyze the sample after adding the correct amount of system monitoring compound and internal standard spiking solutions.

- If the system monitoring compound spiking solution or internal standard compound spiking solution was improperly prepared or concentration and/or degradation has occurred, re-prepare the solutions and reanalyze the samples.

- If the instrument malfunctioned, correct the instrument problem and reanalyze the sample. If the instrument malfunction affected the calibration, recalibrate the instrument as per Section 9.3, before reanalyzing the sample. Verify that the system monitoring compound recoveries meet technical acceptance criteria.

11.4.3.2 If the above actions do not correct the problem, then the problem may be due to a sample matrix effect. To determine if there was a matrix effect, take the following corrective action steps:

- Reanalyze the sample. EXCEPTION: If system monitoring compound recoveries or internal standard compound responses in a sample used for a matrix spike or matrix spike duplicate were outside the technical acceptance criteria, then it should be reanalyzed only if system monitoring compound recoveries and internal standard compound responses met technical acceptance criteria in both the matrix spike and matrix spike duplicate analyses.

- If the system monitoring compound recoveries and/or the internal standard compound responses meet the technical acceptance criteria in the reanalyzed sample, then the problem was within the Contractor's control. The contractor should make every effort to reanalyze the sample within the contract required holding times. If the reanalysis was performed within holding times, then submit data only from the reanalysis. If the reanalysis was performed outside holding times, then submit both sets of data.

- If the system monitoring compound recoveries and/or the internal standard compound responses fail to meet the acceptance windows in the reanalysis, then submit data from both analyses. Distinguish between the initial analysis and the reanalysis on all deliverables using the suffixes on Exhibit B.

11.4.4 Corrective action for system monitoring compound relative retention times and/or internal standard compound retention times outside technical acceptance criteria are defined below.

11.4.4.1 If any of the system monitoring compound relative retention times or internal standard compound retention times are not within their technical acceptance criteria defined in Sections 11.3.6 and 11.3.7, check the instrument for malfunctions. If the instrument malfunctioned, correct the instrument problem and reanalyze the sample. If the instrument malfunction affected the calibration, recalibrate the instrument according to Section 9.3 before reanalyzing the samples.

11.4.4.2 If the above actions do not correct the problem, then the problem may be due to a sample matrix effect. To determine if there was a matrix effect, take the following corrective action steps:

- Reanalyze the sample. EXCEPTION: If the system monitoring compounds relative retention times or internal standard compounds retention times in a sample used for a matrix spike or matrix spike duplicate were outside the technical acceptance criteria, then it should be reanalyzed only if the system monitoring compounds and internal standard compounds retention times were within the acceptance criteria in both the matrix spike and matrix spike duplicate analyses.

- If the system monitoring compounds relative retention times and internal standard compounds retention times are within the acceptance criteria, then the problem was within the Contractor's control. Therefore, submit only data from the reanalysis when the system monitoring compounds relative retention times and the internal standard compounds retention times are within the acceptance limits. If the sample were reanalyzed outside the contract required holding times, then submit both sets of data.

- If the system monitoring compounds relative retention times or the internal standard compounds retention times are outside the acceptance criteria in the reanalysis, then submit data from both analyses. Distinguish between the initial analysis and the reanalysis on all deliverables, using the suffixes in Exhibit B.

11.4.5 If the technical acceptance criteria for GC/MS instrument performance checks, initial calibration, initial calibration verification, continuing calibration, and method/instrument/storage blanks are not met, then the contractor must stop and correct the problem before continuing the analytical sequence. Any samples analyzed when the above technical acceptance criteria have not been met must be reanalyzed at no additional cost to the Agency. Reanalysis must be completed within the contract required holding times and must meet all technical acceptance criteria.

11.4.6 Sample analyses reported with non-compliant GC/MS instrument performance checks, initial calibration, initial calibration verification, continuing calibrations and/or method/instrument/ storage blanks shall be subject to a commensurate reduction in sample price or zero payment due to data rejection, depending upon the impact of the non-compliance on data usability.

12.0 QUALITY CONTROL

12.1 Blank Analyses

12.1.1 Summary -- Sample analyses must not proceed until all blank technical acceptance criteria have been met. There are three different types of blanks required by this method.

12.1.1.1 METHOD BLANK - a volume of a clean reagent water is carried through the entire analytical procedure. The volume of the reagent water must be approximately equal to the volume used for the samples associated with the blank. The purpose of a method blank is to determine the levels of contamination associated with the processing and analysis of samples.

12.1.1.2 STORAGE BLANK - upon receipt of the first samples in an SDG, two 40.0 ml screw-cap volatile vials with a PTFE-faced silicone septa are filled with reagent water (80 ml total). The vials are stored with the samples in the SDG under the same storage conditions. The storage blank is analyzed concurrently with the last sample in the SDG. The storage blank indicates whether contamination may have occurred during storage of samples.

12.1.1.3 INSTRUMENT BLANK - a 5.0 ml (or 25 ml) aliquot of reagent water that is carried through the entire analytical procedure. Instrument blanks are analyzed after a sample or sample dilution which contains any target or non-target compounds that exceed the initial calibration range. The results from the instrument blank analysis indicate whether there is contamination from a previous sample. Instrument blanks must be analyzed to demonstrate that the purge chamber and purge and trap system are free of contamination.

12.1.2 Frequency of Blank Analyses

12.1.2.1 Method Blank - The method blank must be analyzed at least once during every 12-hour time period on each GC/MS system used for volatile analysis (see Section 9.2.2 for the definition of the 12-hour time period).

12.1.2.2 The method blank **must** be analyzed after the continuing calibration and before any samples or QC samples are analyzed. The method blank must be analyzed after the initial calibration sequence if samples are analyzed before the 12-hour period expires. A method blank must be analyzed in each 12-hour time period in which samples, QC samples or required blanks are analyzed.

12.1.2.3 Storage Blank - A minimum of one storage blank must be analyzed concurrently with the last sample in the SDG.

12.1.2.4 Instrument Blank - The Contractor must demonstrate that there is no carryover from contaminated samples before data from subsequent analyses may be used. Samples/dilutions may contain target compounds at levels exceeding the initial calibration range. An instrument blank must be analyzed after the sample that exceeds the calibration range, in the same purge vessel/inlet if an autosampler is used or after a sample that meets the maximum contamination criteria in Section 11.3.8 must be analyzed. For these purposes, if the instrument blank meets the technical acceptance criteria for blank analyses or the sample meets the maximum contamination criteria, the system is considered to be uncontaminated. If the instrument blank or sample does not meet the criteria (i.e., is considered to be contaminated), then the system must be decontaminated. Until an instrument blank meets the blank technical acceptance criteria or a sample meets the maximum contamination criteria in Section 11.3.8, any samples analyzed since the original contaminated sample must be reanalyzed at no additional cost to the Agency. NOTE: Only the instrument blank which demonstrates that there was no carryover from the previous sample or the instrument blank that demonstrates that the system is clean (Section 12.1.4) needs to be reported. Instrument blanks analyzed during the instrument decontamination process which exceed the requirements listed in Section 12.1.4 do not need to be reported.

12.1.3 Procedure for Blank Analyses

12.1.3.1 Method Blank - A volatile method blank consists of a 5 ml (or 25 ml) volume of reagent water (Section 7.1.1) that is spiked with the 5 µl of the appropriate system monitoring compound spiking solution (Section 7.2.4.1) and 5 µl of the appropriate internal standard spiking solution (Section 7.2.4.3) and carried through the analytical procedure.

12.1.3.2 Storage Blank - A storage blanks consist of a 5 ml (or 25 ml) aliquot of reagent water (Section 7.1.1) from one of the 40 ml VOA vials that had been stored with a group of samples from an SDG (Section 12.1.1.2). The storage blank is spiked with 5 µl of the appropriate system monitoring compound spiking solution (Section 7.2.4.1) and 5 µl of the appropriate internal standard spiking solution (Section 7.2.4.3) and carried through the analytical procedure.

12.1.3.3 Instrument Blank - An instrument blank consist of a 5 ml (or 25 ml) volume of reagent water (Section 7.1.1) that is spiked with 5 µl of the appropriate system monitoring compound spiking solution (Section 7.2.4.1) and 5 µl of the appropriate internal standard spiking solution (Section 7.2.4.3) and carried through the analytical procedure.

12.1.3.4 Identify and quantitate target and non-target compounds in all blanks following the procedures outlined in Sections 11.1 and 11.2.

12.1.4 Technical Acceptance Criteria for Blank Analyses

12.1.4.1 All blanks must be analyzed on a GC/MS system meeting the GC/MS instrument performance check, initial calibration, initial calibration verification and continuing calibration technical acceptance criteria as defined in Sections 9.2.4, 9.3.5, 9.4.5 and 9.5.5, respectively. All blanks must be analyzed at the frequency described in Section 12.1.2.

12.1.4.2 The percent recovery of each of the system monitoring compounds in any blank must be within the technical acceptance windows listed in Table 6.

12.1.4.3 The EICP area (or height) response for each of the internal standards in any blank must be within the inclusive range of -50.0 percent and +100.0 percent of the response of the internal standards in the most recent continuing calibration analysis (or 10 µg/L initial calibration standard, if appropriate).

12.1.4.4 The retention time shift for each of the internal standards in any blank must be within ±0.50 minutes (30 seconds) of the retention times of the internal standards in the most recent continuing calibration standard analysis (or 10 µg/L initial calibration standard, if appropriate).

12.1.4.5 The relative retention time (RRT) of the system monitoring compounds in any blank must be within ±0.06 (RRT) units of its relative retention time in the continuing calibration standard (or 10 µg/L initial calibration standard, if appropriate).

12.1.4.6 The concentration of each target compound found in the blank must be less than its CRQL listed in Exhibit C (524.2 Volatiles), except for methylene chloride which must be less than 2.5 times its CRQL, and acetone and 2-butanone, which must be less than 5 times the CRQL.

12.1.4.7 Non-target compounds which are found in the blanks must not interfere with target compound identification or quantitation.

12.1.5 Corrective Action for Blank Analyses

12.1.5.1 It is the Contractor's responsibility to ensure that method interferences caused by the contaminants in solvent, reagents, glassware, laboratory air and other sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be eliminated. If a Contractor's blanks exceed the technical acceptance criteria listed in Section 12.1.4.5, the Contractor must consider the analytical system to be out of control. The source of the contamination must be investigated and appropriate corrective measures must be taken and documented before any further samples or QC samples are analyzed.

12.1.5.2 Any method blank or instrument blank that fails to meet the technical acceptance criteria for blank analyses must be reanalyzed at no additional cost to the Agency. Furthermore, all samples, including QC samples, processed within the 12-hour period associated with a method blank or instrument blank that does not meet the technical acceptance criteria for blanks must be reanalyzed at no additional cost to the Agency.

12.1.5.3 If the storage blank does not meet the technical acceptance criteria for blank analyses listed in Sections 12.1.4.1 through 12.1.4.5, then correct system problems and reanalyze the storage blank. If the storage blank does not meet the technical acceptance criteria listed in Section 12.1.4.6, reanalyze the storage blank to determine whether the contamination occurred during storage or during the analysis. If, upon reanalysis, the storage blank meets the technical acceptance criteria listed in Section 12.1.4, the problem occurred during the analysis and the reanalyzed storage blank results must be reported. If upon reanalysis, the storage blank did not meet the technical acceptance criteria listed in Section 12.1.4.6, the problem occurred during storage. The laboratory manager or his/her designee must address the problem in the SDG Narrative and discuss the corrective actions implemented to prevent future occurrences. Report storage blank results on a Form I, which must meet all requirements in Exhibit B and be included with the data package.

12.1.5.4 If the technical acceptance criteria for blank analyses are not met, then the contractor must stop and correct the problem before continuing the analytical sequence. If sample analyses are reported with non-compliant blanks, then the contractor shall receive a commensurate reduction in sample price or zero payment depending upon the impact of the non-compliance on data usability.

12.2 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

12.2.1 Summary of MS/MSD

In order to evaluate the effects of the sample matrix and to determine the precision of the methods used for volatile analysis, the Agency has prescribed a mixture of volatile target compounds to be spiked into two aliquots of a sample, and analyzed in accordance with the appropriate method.

12.2.2 Frequency of MS/MSD

12.2.2.1 A matrix spike and matrix spike duplicate must be performed for each group of samples of a similar matrix for the following, whichever is most frequent:

- Each SDG (not to exceed 20 field samples), or
- Each matrix within an SDG.
- ! EPA may require additional MS/MSD analyses, upon Regional request, for which the Contractor will be paid.

12.2.2.2 As a part of the Agency's QA/QC program, aqueous equipment and/or trip blanks (field QC) may accompany water samples that are delivered to a laboratory for analysis. The Contractor shall not perform MS/MSD analysis on any of the field QC samples.

12.2.2.3 The Contractor shall not perform MS/MSD analysis on any designated Performance Evaluation samples.

12.2.2.4 If the EPA Region designates a sample to be used as an MS/MSD, then that sample must be used. If there is insufficient sample volume to perform an MS/MSD, then the Contractor shall contact the RSCC to ascertain an alternate sample to be used for the MS/MSD analysis. The EPA sample numbers, the Region's instructions, and the date of contact must be included in the SDG Narrative.

12.2.2.5 If there is insufficient sample volume in any of the samples in an SDG to perform an MS/MSD, then the Contractor shall immediately contact the RSCC to report the problem. The Region will either approve that no MS/MSD is required, or require that a reduced sample aliquot be used for the unspiked sample and MS/MSD analysis, or that the unspiked sample is analyzed at full volume and the MS/MSD is analyzed at reduced volume. The RSCC will notify the Contractor of the resolution. The Contractor shall document the decision in the SDG Narrative.

12.2.2.6 If the Contractor has a question regarding the frequency, etc., of the MS/MSD analyses for a particular SDG, contact the RSCC for clarification.

12.2.3 Procedure for Preparing MS/MSD

12.2.3.1 To prepare a matrix spike and matrix spike duplicate, add 5 µl of the appropriate matrix spike solution (Section 7.2.4.2) to each of the 5 ml (or 25 ml) aliquots of the sample chosen for spiking. Process samples according to Sections 10.1.3.7 through 10.1.3.8. Disregarding any dilutions, this is equivalent to a concentration of 25 µg/L of 2- Hexanone, 250 µg/L Tetrahydrofuran and 10 µg/L of each of the remaining matrix spike compounds.

12.2.3.1.1 Before performing an MS/MSD analysis, analyze the sample used for MS/MSD. If the sample analysis required dilution, the aliquots for the MS/MSD can be prepared at the same dilution as the least diluted analysis for which the sample results will be reported to the Agency. Sample dilutions must be performed in accordance with Section 10.1.3. Do **not** further dilute MS/MSD samples to get **either** spiked **or** non-spiked analytes within calibration range.

12.2.4 Calculations for MS/MSD

12.2.4.1 Calculate the concentrations of the matrix spike compounds using equation 5.

12.2.4.2 Calculate the recovery of each matrix spike compound using the following equation:

EQ. 8

$$Matrix\ Spike\ Recovery = \frac{SSR - SR}{SA} \times 100$$

Where,

SSR = Spiked sample result
SR = Sample result
SA = Spike added

12.2.4.3 Calculate the relative percent difference (RPD) of the recoveries of each compound in the matrix spike and matrix spike duplicate as follows:

EQ. 9

$$RPD = \frac{|MSR - MSDR|}{\frac{1}{2}(MSR + MSDR)} \times 100$$

Where,

MSR = Matrix spike recovery
MSDR = Matrix spike duplicate recovery

The vertical bars in the formula above indicate the absolute value of the difference, hence RPD is always expressed as a positive value.

12.2.5 Technical Acceptance Criteria for MS/MSD

12.2.5.1 All MS/MSDs must be analyzed on a GC/MS system meeting the GC/MS instrument performance check, initial calibration, initial calibration verification, and continuing calibration technical acceptance criteria defined in Sections 9.2.4, 9.3.5, 9.4.5 and 9.5.5, respectively. The MS/MSD must be analyzed at the frequency described in Section 12.2.2.

12.2.5.2 The MS/MSDs must be analyzed or reanalyzed within the contract required holding time defined in Section 8.3.

12.2.5.3 All MS/MSDs must have associated method blanks, storage blanks, and instrument blanks meeting the blank technical acceptance criteria defined in Section 12.1.4.

12.2.5.4 The percent recovery of each of the system monitoring compounds in the MS/MSDs must be within the technical acceptance windows listed in Table 6.

12.2.5.5 The EICP area (or height) response for each of the internal standards in any blank must be within the inclusive range of -50.0 percent and +100.0 percent of the response of the internal standards in the most recent continuing calibration analysis (or 10 µg/L initial calibration standard, if appropriate).

12.2.5.6 The retention time shift for each of the internal standards in any blank must be within ±0.50 minutes (30 seconds) of the retention times of the internal standards in the most recent continuing calibration standard analysis (or 10 μg/L initial calibration standard, if appropriate).

12.2.5.7 The relative retention time (RRT) of the system monitoring compounds in any blank must be within ±0.06 (RRT) units of its relative retention time in the continuing calibration standard (or 10 μg/L initial calibration standard, if appropriate).

12.2.5.8 Excluding those ions in the solvent front, no ion from a target or non-target compound may saturate the detector. No target compound concentration may exceed the upper limit of the initial calibration range unless a diluted aliquot of the sample is also analyzed according to the procedures in Section 10.1.3.

12.2.5.9 The technical acceptance criteria for MS/MSD compound recoveries and RPD are given in Table 7. As these limits are only advisory, no further action by the laboratory is required. However, frequent failures to meet the limits for recovery or RPD warrant investigation by the laboratory, and may result in questioning from the Agency.

12.2.6 Corrective Action for MS/MSD

Any MS/MSD that does not meet the technical acceptance criteria for MS/MSD must be reanalyzed at no additional cost to the Agency. Both sets of data must be reported.

12.2.6.1 Corrective actions for failure to meet GC/MS instrument performance check, initial calibration, initial calibration verification and continuing calibration must be completed before the analysis of any QC samples.

12.2.6.2 Corrective actions for failure to meet blank technical acceptance criteria must be met before the analysis of any QC samples.

12.2.6.3 Corrective actions for system monitoring compound recoveries and/or internal standard compound responses defined in Section 11.4.3 must be completed before QC sample results are reported.

12.2.6.4 Corrective actions for system monitoring compound relative retention times and/or internal standard compound retention times defined in Section 11.4.4 must be completed before QC sample results are reported.

12.2.6.5 If the technical acceptance criteria for the MS/MSD analyses are not met, then the contractor shall determine whether the non-compliance is due to the sample matrix, the sample preparation or GC system problems.

12.2.6.6 To determine if the non-compliance is due to sample preparation or GC system problems, check calculations, sample preparation logs, the matrix spiking solution, and the instrument operation. If the calculations were incorrect, correct the calculations and verify the MS/MSD recoveries. If the sample preparation logs indicate that the incorrect amount of matrix spiking solution was added, then re-prepare/re-extract and reanalyze the MS/MSD after adding the correct amount of matrix spiking solution. If the matrix spiking solution was improperly prepared, concentrated, or degraded, re-prepare the solution and re-prepare/re-extract and reanalyze the MS/MSD. If the instrument malfunctioned, correct the instrument problem and reanalyze the MS/MSD. Re-verify all MS/MSD recoveries. If the instrument malfunction affected the calibrations, recalibrate the instrument before reanalyzing the MS/MSD.

12.2.6.7 If the above actions do not correct the problem, then the problem may be due to a sample matrix effect. To determine if there was a matrix effect, take the following corrective action steps:

- Reanalyze the MS/MSD samples.
- If the MS/MSD recoveries meet the technical acceptance criteria in the reanalyzed sample, then the problem was within the Contractor's control. The contractor should make every

effort to reanalyze the sample within the contract required holding times. If the reanalysis was performed within holding times, then submit data only from the reanalysis. If the reanalysis was performed outside holding times, then submit both sets of data.

- If the MS/MSD recoveries fail to meet the acceptance criteria in the reanalysis, then submit data from both analyses. Distinguish between the initial analysis and the reanalysis on all deliverables using the suffixes described in Exhibit B.

12.3 SDG-Specific Performance Evaluation (PE) Samples

12.3.1 Summary of SDG-Specific PE Samples

The Region I Performance Evaluation (PE) program has two functions, (1) to evaluate laboratory operation and protocols over a period of time, and (2) to provide information on the quality of individual data packages.

12.3.2 Frequency of SDG-Specific PE Samples

12.3.2.1 The Region will submit PE samples with every SDG, per parameter (as available). The Region may obtain these SDG-Specific PE samples from either a commercial vendor or from the CLP National Program Office (NPO) which provides PE samples in support of the Superfund program. PE samples provided by the CLP-NPO are referred to as "EPA generated".

12.3.2.2 When the Region submits an aqueous PE sample with aqueous field samples, then the Contractor shall not choose the PE sample for MS/MSD analysis.

12.3.2.3 If the PE sample is received as an ampulated standard extract, the ampulated PE sample is not considered to be another matrix type.

12.3.3 Procedure for Preparing SDG-Specific PE Samples

12.3.3.1 Instructions for preparation of the PE samples will be included with each submission of PE samples.

12.3.3.2 If PE sample directions do not apply to a PE sample received, then the Contractor must contact the RSCC to ascertain whether or not to analyze the PE sample and to obtain appropriate PE sample directions.

12.3.4 Calculations for SDG-Specific PE Samples

For EPA-generated and commercially prepared PE samples that are submitted with each SDG, the Contractor must correctly identify and quantitate all TCL compounds using the criteria presented in Section 11.0 - Data Analysis and Calculations.

12.3.5 Technical Acceptance Criteria for SDG-Specific PE Samples

12.3.5.1 All SDG-Specific PE samples must be analyzed under the same GC/MS conditions set up in Section 9.0 and must meet the same technical acceptance criteria established for sample analysis defined in Section 11.3.

12.3.5.2 EPA-generated PE samples included with the SDG will be evaluated by the Region using a CLP NPO computer program called PeacTOOLs. PeacTOOLs rates the PE sample results based on statistically generated confidence intervals.

12.3.5.3 The results of commercially prepared PE samples will be evaluated using the vendors' statistically generated confidence intervals.

12.3.5.4 Contractor results for the SDG-Specific PE samples will be evaluated using the most recent Region I data validation criteria for PE samples.

12.3.5.5 At a minimum, the PE results will be evaluated for compound identification, quantitation, and sample contamination. Confidence intervals for the quantitation of target compounds are based on reported values using population statistics. The Agency may adjust the criteria on any given PE sample to compensate for unanticipated difficulties with a particular sample. Normally, a fraction of the compounds spiked into the sample are not specifically listed in the contract. Contractors must use the guidelines described in Section 11.2.2 for identification of non-target compounds. Tentative identification of these non-target compounds is evaluated and integrated into the evaluation process.

12.3.6 Corrective Action for SDG-Specific PE Samples

12.3.6.1 The corrective actions for PE sample results which do not meet the technical acceptance criteria defined in Section 12.3.5.1 above are the same corrective actions outlined for sample analysis in Section 11.4.

12.3.6.2 If an SDG Specific PE sample evaluated by Region I as described in Sections 12.3.5.2 through 12.3.5.5 above, indicates unacceptable laboratory performance, then the Contractor may be required to reanalyze all samples, standards, blanks and QC samples associated with the unacceptable PE sample result (if sufficient volume remains) and/or analyze a new PE sample at no additional cost to the Agency. Unacceptable laboratory performance includes either a TCL false positive result, false negative result, and/or compound misquantitation (reported result exceeds $\pm$ 3 sigma of the spiked compound concentration).

12.3.6.3 Sample results reported with unacceptable SDG specific PE results shall be subject to a commensurate reduction in sample price or zero payment due to data rejection, depending upon the impact of the non-compliance on data usability.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions.

16.0 REFERENCES

1. U.S. EPA Method 524.2, "Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectroscopy", Revision 4, EPA Document #: EPA/600/4-88/039, 1992.

2. U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, Revision OLM03.1, EPA-540/R-94/073, August, 1994.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

Table 1

BFB Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
50	8.0-40.0 percent of mass 95
75	30.0-66.0 percent of mass 95
95	base peak, 100 percent relative abundance
96	5.0-9.0 percent of mass 95 (see note)
173	less than 2.0 percent of mass 174
174	50.0-120.0 percent of mass 95
175	4.0-9.0 percent of mass 174
176	93.0-101.0 percent of mass 174
177	5.0-9.0 percent of mass 176

NOTE: All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120.0 percent that of m/z 95.

Table 2

Characteristic Ions for Volatile Target Compounds

Analyte	Primary Quantitation Ion	Secondary Ion(s)
Dichlorodifluoromethane	85	87
Chloromethane	50	52
Vinyl Chloride	62	64
Bromomethane	94	96
Chloroethane	64	66
Trichlorofluoromethane	101	103
1,1-Dichloroethene	96	61, 63
Acetone	43	58
Carbon Disulfide	76	78
Methylene chloride	84	49, 86
trans-1,2-Dichloroethene	96	61, 98
1,1-Dichloroethane	63	65, 83
2,2-Dichloropropane	77	97
2-Butanone	43*	57, 72
cis-1,2-Dichloroethene	96	61, 98
Chloroform	83	85
Bromochloromethane	128	49, 130
1,1,1-Trichloroethane	97	99, 61
1,1-Dichloropropene	75	110, 77
Carbon Tetrachloride	117	119
Benzene	78	77
1,2-Dichloroethane	62	98
Trichloroethene	95	130, 132
1,2-Dichloropropane	63	112
Bromodichloromethane	83	85, 127
Dibromomethane	93	95, 174
4-Methyl-2-Pentanone	43	58, 85
trans-1,3-Dichloropropene	75	110
Toluene	92	91
cis-1,3-Dichloropropene	75	110
1,1,2-Trichloroethane	83	97, 85
2-Hexanone	43	58
Tetrachloroethene	164	129, 166
1,4-Dioxane	88	58, 43
Tetrahydrofuran	71	72, 42
1,3-Dichloropropane	76	78

Table 2 (continued)

Analyte	Primary Quantitation Ion	Secondary Ion(s)
Dibromochloromethane	129	127
Bromoform	173	175, 252
Isopropylbenzene	105	120
1,2-Dibromoethane	107	109, 188
Chlorobenzene	112	77, 114
Ethylbenzene	91	106
1,1,1,2-Tetrachloroethane	131	133, 119
1,1,2,2-Tetrachloroethane	83	131, 85
Xylenes	106	91
Styrene	104	78
Bromobenzene	156	77, 158
N-Propylbenzene	91	120
1,2,3-Trichloropropane	75	77
2-Chlorotoluene	91	126
1,3,5-Trimethylbenzene	105	120
4-Chlorotoluene	91	126
tert-Butylbenzene	119	91
1,2,4-Trimethylbenzene	105	120
sec-Butylbenzene	105	134
4-Isopropyltoluene	119	134, 91
1,3-Dichlorobenzene	146	111, 148
1,4-Dichlorobenzene	146	111, 148
N-Butylbenzene	91	134
1,2-Dichlorobenzene	146	111, 148
1,2-Dibromo-3-Chloropropane	75	155, 157
1,2,4-Trichlorobenzene	180	182
Hexachlorobutadiene	225	260
Naphthalene	128	--
1,2,3-Trichlorobenzene	180	182

[*] m/z 43 is used for quantitation of 2-Butanone, but m/z 72 **must** be present for positive identification.

Table 3

Volatile Internal Standards with Corresponding Target Compounds and System Monitoring Compounds Assigned for Quantitation

Fluorobenzene	Chlorobenzene-d_5
Dichlorodifluorobenzene	Dibromochloromethane
Chloromethane	Bromoform
Vinyl Chloride	Isopropylbenzene
Bromomethane	1,2-Dibromoethane
Chloroethane	Chlorobenzene
Trichlorofluoromethane	Ethylbenzene
1,1-Dichloroethene	1,1,1,2-Tetrachlorobenzene
Acetone	1,1,2,2-Tetrachlorobenzene
Carbon Disulfide	Xylenes
trans-1,2-Dichloroethene	Styrene
1,1-Dichloroethane	Bromobenzene
2,2-Dichloropropane	N-Propylbenzene
2-Butanone	1,2,3-Trichloropropane
cis-1,2-Dichloroethene	2-Chlorotoluene
Chloroform	1,3,5-Trimethylbenzene
Bromochloromethane	4-Chlorotoluene
1,1,1-Trichloroethane	tert-Butylbenzene
1,1-Dichloropropene	1,2,4-Trimethylbenzene
Carbon Tetrachloride	sec-Butylbenzene
Benzene	4-Isopropyltoluene
1,2-Dichloroethane	1,3-Dichlorobenzene
Trichloroethene	1,4-Dichlorobenzene
1,2-Dichloropropane	N-Butylbenzene
Bromodichloromethane	1,2-Dichlorobenzene
Dibromomethane	1,2-Dibromo-3-Chloropropane
4-Methyl-2-Pentanone	1,2,4-Trichlorobenzene
trans-1,3-Dichloropropene	Hexachlorobutadiene
Toluene	Naphthalene
cis-1,3-Dichloropropene	1,2,3-Trichlorobenzene
1,1,2-Trichloroethane	1,2-Dichlorobenzene-d4 (SMC)
2-Hexanone	
Tetrachloroethene	
1,4-Dioxane	
Tetrahydrofuran	
1,3-Dichloropropane	
1,2-Dichloroethane-d4 (SMC)	

(SMC) = system monitoring compound

Table 4

Characteristic Ions for System Monitoring Compounds and Internal Standards for Volatile Organic Compounds with CAS Numbers

Compound	Primary Quantitation Ion	Secondary Ion(s)
SYSTEM MONITORING COMPOUNDS		
1,2-Dichloroethane-d4	65	67, 102
1,2-Dichlorobenzene-d4	152	115, 150
INTERNAL STANDARDS		
Fluorobenzene	96	77
Chlorobenzene-d_5	117	82, 119

Table 5

Relative Response Factor Criteria for Initial and Continuing Calibration of Volatile Organic Compounds

Volatile Compound	Minimum RRF	Maximum %RSD	Maximum %Diff
Dichlorodifluoromethane	0.050	≤25.0	±30.0
Chloromethane	0.050	≤25.0	±30.0
Vinyl Chloride	0.050	≤25.0	±30.0
Bromomethane	0.050	≤25.0	±30.0
Chloroethane	0.050	≤25.0	±30.0
Trichlorofluoromethane	0.050	≤25.0	±30.0
1,1-Dichloroethene	0.050	≤25.0	±30.0
Acetone	0.020	≤25.0	±30.0
Carbon Disulfide	0.050	≤25.0	±30.0
Methylene Chloride	0.050	≤25.0	±30.0
trans-1,2-Dichloroethene	0.050	≤25.0	±30.0
1,1-Dichloroethane	0.050	≤25.0	±30.0
2,2-Dichloropropane	0.050	≤25.0	±30.0
2-Butanone	0.010	≤25.0	±30.0
cis-1,2-Dichloroethene	0.050	≤25.0	±30.0
Chloroform	0.050	≤25.0	±30.0
Bromochloromethane	0.020	≤25.0	±30.0
1,1,1-Trichloroethane	0.050	≤25.0	±30.0
1,1-Dichloropropene	0.050	≤25.0	±30.0
Carbon Tetrachloride	0.050	≤25.0	±30.0
Benzene	0.050	≤25.0	±30.0
1,2-Dichloroethane	0.050	≤25.0	±30.0
Trichloroethene	0.050	≤25.0	±30.0
1,2-Dichloropropane	0.050	≤25.0	±30.0
Bromodichloromethane	0.050	≤25.0	±30.0
Dibromomethane	0.020	≤25.0	±30.0
4-Methyl-2-Pentanone	0.020	≤25.0	±30.0
trans-1,3-Dichloropropene	0.050	≤25.0	±30.0
Toluene	0.050	≤25.0	±30.0
cis-1,3-Dichloropropene	0.050	≤25.0	±30.0
1,1,2-Trichloroethane	0.050	≤25.0	±30.0
2-Hexanone	0.020	≤25.0	±30.0
Tetrachloroethene	0.050	≤25.0	±30.0
1,4-Dioxane	none	≤25.0	±30.0
Tetrahydrofuran	0.020	≤25.0	±30.0
1,3-Dichloropropane	0.050	≤25.0	±30.0

Table 5 (continued)

Volatile Compound	Minimum RRF	Maximum %RSD	Maximum %Diff
Dibromochloromethane	0.020	≤25.0	±30.0
Bromoform	0.020	≤25.0	±30.0
Isopropylbenzene	0.050	≤25.0	±30.0
1,2-Dibromomethane	0.020	≤25.0	±30.0
Chlorobenzene	0.050	≤25.0	±30.0
Ethylbenzene	0.050	≤25.0	±30.0
1,1,1,2-Tetrachloroethane	0.050	≤25.0	±30.0
1,1,2,2-Tetrachloroethane	0.050	≤25.0	±30.0
Xylenes	0.050	≤25.0	±30.0
Styrene	0.050	≤25.0	±30.0
Bromobenzene	0.050	≤25.0	±30.0
N-Propylbenzene	0.050	≤25.0	±30.0
1,2,3-Trichloropropane	0.050	≤25.0	±30.0
2-Chlorotoluene	0.050	≤25.0	±30.0
1,3,5-Trimethylbenzene	0.050	≤25.0	±30.0
4-Chlorotoluene	0.050	≤25.0	±30.0
tert-Butylbenzene	0.050	≤25.0	±30.0
1,2,4-Trimethylbenzene	0.050	≤25.0	±30.0
sec-Butylbenzene	0.050	≤25.0	±30.0
4-Isopropyltoluene	0.050	≤25.0	±30.0
1,3-Dichlorobenzene	0.050	≤25.0	±30.0
1,4-Dichlorobenzene	0.050	≤25.0	±30.0
N-Butylbenzene	0.050	≤25.0	±30.0
1,2-Dichlorobenzene	0.050	≤25.0	±30.0
1,2-Dibromo-3-Chloropropane	0.020	≤25.0	±30.0
1,2,4-Trichlorobenzene	0.050	≤25.0	±30.0
Hexachlorobutadiene	0.050	≤25.0	±30.0
Naphthalene	0.050	≤25.0	±30.0
1,2,3-Trichlorobenzene	0.050	≤25.0	±30.0
SYSTEM MONITORING COMPOUNDS			
1,2-Dichlorobenzene-d4	0.050	≤25.0	±30.0
1,2-Dichloroethane-d4	0.050	≤25.0	±30.0

Table 6

System Monitoring Compound Recovery Limits

Compound	% Recovery Water
1,2-Dichloroethane-d4	80-120
1,2-Dichlorobenzene-d4	80-120

Table 7

Matrix Spike Recovery and
Relative Percent Difference Limits

Compound	% Recovery Water	RPD Water
Vinyl Chloride	80-120	20
Trichloroethene	80-120	20
1,2-Dichloroethane	80-120	20
Carbon Tetrachloride	80-120	20
Benzene	80-120	20
1,2-Dichloropropane	80-120	20
Bromoform	80-120	20
1,2,3-Trichloroethane	80-120	20
cis-1,3-Dichloropropene	80-120	20
Tetrachloroethene	80-120	20
1,2-Dibromomethane	80-120	20
1,4-Dichlorobenzene	80-120	20
2-Hexanone	80-120	20
Tetrahydrofuran	80-120	20